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CONTENTS.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Full Title.
A.	Abstracts in Journal of the Chemical Society (until 1925) or in British Chemical Abstracts,* Section A.
Abs. Theses Mass. Inst. Tech.	Abstracts of scientific and technical publications, including abstracts of Doctors' theses, of the Massachusetts Institute of Technology.
Abs. Theses Univ. Chicago. (Sci Ser.) . . .	Abstracts of Theses, University of Chicago (Science Series).
Amer. J. Bot. . . .	American Journal of Botany.
Amer. J. Pharm. . .	American Journal of Pharmacy.
Amer. J. Physiol. . .	American Journal of Physiology.
Amer. J. Sci. . . .	American Journal of Science.
Amer. Min. . . .	American Mineralogist.
Anal. Asoc. Quím Argentina	Anales de la Asociacíon Química Argentina.
Anal. Fís. Quím. . .	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Annalen . . .	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim. . . .	Annales de Chimie.
Ann. Chim. Appl. . .	Annali di Chimica Applicata.
Ann. Jard. bot. Buitenzorg.	Annales du Jardin botanique de Buitenzorg.
Ann. Physik . . .	Annalen der Physik.
Ann. Physique . . .	Annales de Physique.
Ann. Reports . . .	Annual Reports of the Chemical Society.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. Pharm. . . .	Archiv der Pharmazie.
Arhiv Hemiju . . .	Arhiv za Hemiju i Farmaciju.
Atti II Cong. Naz. Chim. pura appl. . .	Atti del IIº Congress Nazionale di Chimica pura ed applicata.
Atti R. Accad. Lincei .	Atti (Rendiconti, Memorie) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
B.	British Chemical Abstracts,* Section B.
Ber. deut. pharm. Ges. .	Berichte der deutschen pharmazeutischen Gesellschaft.
Ber.	Berichte der deutschen Chemischen Gesellschaft.
Ber. Sächs. Akad. Wiss. .	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Ber. ungar. pharm. Ges. .	Berichte der ungarischen pharmazeutischen Gesellschaft.
Biochem. J. . . .	The Biochemical Journal.
Biochem. Z. . . .	Biochemische Zeitschrift.
Brit. J. Radiol. . .	The British Journal of Radiology.
Bul. Soc. Chim. România .	Buletinul Sociotätei de Chimie din România.
Bul. Soc. Stiinte Cluj. .	Buletinul Societătii Stiinte din Cluj.
Bull. Acad. Polonaise .	Bulletin Internationale de l' Académie Polonaise des Sciences et des Lettres.
Bull. Chem. Soc. Japan .	Bulletin of the Chemical Society of Japan.
Bull. Inst. Phys. Chem. Res. Tokyo . . .	Bulletin of the Institute of Physical and Chemical Research, Tokyo.
Bull. Nat. Res. Council .	Bulletin of the National Research Council, Washington.
Bull. Soc. chim. .	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg. .	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol. .	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min. .	Bulletin de la Société française de Minéralogie.
Bur. Stand. J. Res. . .	Bureau of Standards Journal of Research.
Canadian Chem. Met. . .	Canadian Chemistry and Metallurgy.
Casopis Ceskoslov. Lék. .	Časopis Českého Lékárnictva.

* The year is not inserted in references to 1929.

Abbreviated Title.	FULL TITLE.
Centr. Min. . . .	Centralblatt für Mineralogie, Geologie, und Paläontologie.
Chem. and Ind. . . .	Chemistry and Industry.
Chem. Erde . . .	Chemie der Erde.
Chem. Listy . . .	Chemické Listy pro Vĕdu a Prŭmysl. Organ de la "Ceská chemická Spoleĕnost pro Vĕdu a Prŭmysl."
Chem. Met. Eng. . .	Chemical and Metallurgical Engineering.
Chem. News . . .	Chemical News.
Chem. Reviews . . .	Chemical Reviews.
Chem. Weekblad . .	Chemisch Weekblad.
Chem. Zentr. . . .	Chemisches Zentralblatt.
Chem.-Ztg. . . .	Chemiker-Zeitung.
Chim. et Ind. . . .	Chimie et Industrie.
Chinese J. Physiol. . .	Chinese Journal of Physiology.
Compt. rend. . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol. .	Comptes rendus hebdomadaires de Séances de la Société de Biology.
Conn. Agric. Exp. Sta. Bull.	Bulletin of the Connecticut Agricultural Experiment Station.
Deut. Z. ges. gerichtl. Med. .	Deutsche Zeitschrift für die gesammte gerichtliche Medizin.
Econ. Geol. . . .	Economic Geology.
Förh. III nord. Kemistmötet	Förhandlingar III Nordiska Kemistmötet.
Fortschr. Min. Krist. Petr.	Fortschritte der Mineralogie, Kristallographie und Petrographie.
Gazzetta	Gazzetta chimica italiana.
Handl. Ing. Vetenskapsaksakad. Stockholm . .	Ingeniörsvetenskapsakadamiens Haudlingar, Stockholm.
Helv. Chim. Acta . .	Helvetica Chimica Acta.
Helv. Phys. Acta . .	Helvetica Physica Acta.
Ind. Eng. Chem. . .	Industrial and Engineering Chemistry.
Indian J. Med. Res. . .	Indian Journal of Medical Research.
Indian J. Physics . .	Indian Journal of Physics.
J.	Journal of the Chemical Society.
J. Agric. Res. . . .	Journal of Agricultural Research.
J. Amer. Chem. Soc. . .	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Pharm. Assoc. .	Journal of the American Pharmaceutical Association.
J. Bact.	Journal of Bacteriology, Baltimore.
J. Biol. Chem. . . .	Journal of Biological Chemistry.
J. Chem. Ind. Moscow .	Journal of Chemical Industry, Moscow.
J. Chem. Met. Min. Soc. S. Africa . . .	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chim. physique . .	Journal de Chimie physique.
J. Czech. Chem. Comm. .	Journal of Czechoslovak Chemical Communications.
J. Exp. Med. . . .	Journal of Experimental Medicine.
J. Gen. Physiol. . .	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Indian Chem. Soc. . .	Quarterly Journal of the Indian Chemical Society.
J. Indian Inst. Sci. . .	Journal of the Indian Institute of Science.
J. Inst. Brewing . .	Journal of the Institute of Brewing.
J. Inst. Metals . .	Journal of the Institute of Metals.
J. Iron Steel Inst. . .	Journal of the Iron and Steel Institute.
J. Pharm. Chim. . .	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther. .	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan. .	Journal of the Pharmaceutical Society of Japan, (Yakugakuzasshi).

Abbreviated Title.	FULL TITLE.
J. Phys. Radium . .	Journal de Physique et le Radium.
J. Physical Chem. .	Journal of Physical Chemistry.
J. pr. Chem. . . .	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal	Journal and Proceedings of the Asiatic Society of Bengal.
J. Roy. Soc. W. Australia .	Journal of the Royal Society of West Australia.
J. Russ. Phys. Chem. Soc. .	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind. . .	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan .	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades Chemists.
Jahrb. Min., Beil-Bd. . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
Japan. J. Chem. . .	Japanese Journal of Chemistry.
Japan. J. Physics . .	Japanese Journal of Physics.
Klin. Woch. . . .	Klinische Wochenschrift.
Kolloidchem. Beih. . .	Kolloidchemische Beihefte.
Kolloid-Z. . . .	Kolloid-Zeitschrift.
Lunds Univ. Årsskr. .	Lunds Universitets Års-skrift.
Mem. Coll. Sci. Kyoto . .	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mikrochem. . . .	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Münch. med. Woch. . .	München medizinische Wochenschrift.
Nach. Ges. Wiss. Göttingen.	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss. . . .	Die Naturwissenschaften.
Natuurwetensch. Tijds. .	Natuurwetenschappelijk Tijdschrift.
New Phyt. . . .	New Phytologist.
Norsk Geol. Tidsskrift .	Norsk Geologisk Tidsskrift, Oslo.
Nov. Act. Reg. Soc. Upsala .	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Oesterr. Chem.-Ztg. . .	Oesterreichische Chemiker-Zeitung.
Papier-Fabr. . .	Papier-Fabrikant.
Pharm. Weekblad. . .	Pharmaceutisch Weekblad.
Pharm. Zentr. . . .	Pharmazeutische Zentralhalle.
Pharm.-Ztg. . . .	Pharmazeutische Zeitung.
Phil. Mag. . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . . .	Philosophical Transactions of the Royal Society of London.
Physical Rev. . . .	Physical Review.
Physikal. Z. . . .	Physikalische Zeitschrift.
Plant Physiol. . . .	Plant Physiology.
Proc. Imp. Acad. Tokyo .	Proceedings of the Imperial Academy of Japan.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Leeds Phil. Soc. .	Proceedings of the Leeds Philosophical and Literary Society (Scientific Section).
Proc. Nat. Acad. Sci. . .	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Physical Soc. . .	Proceedings of the Physical Society of London.
Proc. Roy. Dublin Soc. .	Proceedings of the Royal Dublin Society.
Proc. Roy. Inst. . .	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad. .	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc. . . .	Proceedings of the Royal Society.

A*

Abbreviated Title.			FULL TITLE.
Przemysł Chem.	.	.	Przemysł Chemiczny.
Quart. J. Pharm.		.	Quarterly Journal of Pharmacy and Pharmacology.
Rec. trav. bot. Néerlandaises			Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim.	.	.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	.	.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rev. Centr. Est. Farm. Bioquim.	.	.	Revista del Centro Estudiantes de Farmacia y Bioquimica, Buenos Aires.
Riv. Ital. Ess. Prof.	.	.	Rivista Italiana delle Essenze e Profumi.
Rocz. Chem.	.	.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Schweiz. Apoth.-Ztg.	.	.	Schweizerische Apotheker-Zeitung.
Schweiz. Min. Petr. Mitt.	.	.	Schweizerische mineralogische und petrographische Mitteilungen.
Sci. Papers Inst. Phys. Chem. Res. Tokyo		.	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Rep. Tôhoku Imp. Univ.			Science Reports, Tôhoku Imperial University.
Sitzungsber. Preuss. Akad. Wiss. Berlin	.	.	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skrifter Norske Vidensk. Akad. Oslo	.	.	Skrifter udg. af Videnskabsselskabet i Oslo (I. Matem.-naturvid. Klasse).
Süddeut. Apoth.-Ztg.	.	.	Süddeutsche Apothekerzeitung.
Svensk Kem. Tidskr.	.	.	Svensk Kemisk Tidskrift.
Tech. Rep. Tôhoku Imp. Univ.	.	.	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
Tekn. Tidskr.	.	.	Teknisk Tidskrift.
Tidsskr. Kjemi Berg.	.	.	Tidsskrift for Kemi og Bergvaesen.
Trans. Amer. Electrochem. Soc.	.	.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	.	.	Transactions of the Faraday Society.
Trans. Geol. Soc. S. Africa.		.	Transactions of the Geological Society of South Africa.
Trans. Inst. Pure Chem. Reagents, Moscow.	.	.	Transactions of the Institute for Pure Chemical Reagents, Moscow.
Trans. Roy. Soc. Canada		.	Transactions of the Royal Society of Canada.
Tsch. Min. Petr. Mitt.		.	Tschermaks mineralogische und petrographische Mitteilungen.
Ukraine Chem. J.	.	.	Ukrainian Chemical Journal.
U.S. Bur. Stand. Res. Paper			Research Papers of the U.S. Bureau of Standards.
Wiss. Veröff. Siemens-Konz.			Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Z. anal. Chem.	.	.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	.	.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	.	.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Elektrochem.	.	.	Zeitschrift für Elektrochemie.
Z. Krist.	.	.	Zeitschrift für Krystallographie.
Z. Metallk.	.	.	Zeitschrift für Metallkunde.
Z. Physik	.	.	Zeitschrift für Physik.
Z. physikal. Chem.	.	.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	.	.	Hoppe-Sevler's Zeitschrift für physiologische Chemie.
Z. wiss. Biol.	.	.	Zeitschrift für wissenschaftliche Biologie.

ERRATUM.

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31   19   *delete* "S. Glasstone,⁷⁸."

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ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

THE output of research in this branch of science has been well maintained during the year under review and steady progress has been made. Perhaps the most notable advances of the last year or so have been in the domain of sub-atomic phenomena and molecular structure : we are now observing the confluence of many lines of work, and it is perhaps not too much to say that the elucidation of the chemical significance of molecular structure is progressing with greater rapidity than ever before. The first two sections of this Report are devoted to this subject and a few other topics of interest are touched on later.

The Atom and its Constituent Parts.

One of the outstanding features of recent research has been the introduction, by L. de Broglie,[1] E. Schrödinger,[2] and others, of a theory of wave mechanics according to which a moving particle (in particular, an electron) behaves as a group of waves whose velocity and wave-length are governed by the speed and the mass of the particle. For a particle moving in free space, the theory leads to the equations $\lambda = h\sqrt{1 - v^2/c^2}/m_0v$ and $V = c^2/v$, where λ denotes the wave-length; v, c, and V represent the velocities of the particle, of light, and of the wave front, respectively; h is Planck's constant of action; and m_0 is the mass of the particle at slow speeds. It follows that V is greater than the velocity of light, but since the waves are not considered to carry energy, no contradiction of the deductions of the theory of relativity is involved. In the neighbourhood of matter, the velocity of the wave front is modified and

[1] *Ann. Physique*, 1925, **3**, 22; *J. Phys. Radium*, 1927, [vi], **8**, 225; *A.*, 1927, 807.

[2] *Ann. Physik*, 1926, **79**, 361, 489, 734; **80**, 437; **81**, 109; *Naturwiss.*, 1926, **14**, 664; *Physical Rev.*, 1926, **28**, 1049.

the resultant refraction of the wave corresponds to the modification of the path of the particle when entering the field of force associated with the matter.

A. S. Eddington[3] has raised a question which has aroused very considerable interest. The ratio of hc to e^2 is dimensionless, where e is the charge on an electron. The methods of what may now be termed classical quantum physics (as, for example, in Bohr's theory of atomic structure and spectra) break up this number into constituent factors so that its dimensionless character seems unimportant; but in the wave equation for two electrons (or an electron and a proton) the combination $hc/2\pi e^2$ occurs as the coefficient of certain terms. By conceiving a wider principle of relativity, this author determines the numerical value of this ratio as 136, the number of degrees of freedom appropriate to a two-electron system in 16-space. Although there is some uncertainty about this number, yet it is one of hesitation between, say, 10 and 136 and 256, and not between 136 and 137; but the accepted values for h, c, and e give 137·1 as the magnitude of the ratio. (It is said, however, that a new determination of e by Siegbahn has given the value $4·792 \times 10^{-10}$ c.g.s.e.s.u. as against R. A. Millikan's value of $4·774 \times 10^{-10}$.) That there is a real uncertainty as to the magnitude of e within the limits indicated by Eddington's theory, is pointed out by E. Bäcklin,[4] who, after examining the values obtained by Millikan, Wadlund, and himself, concludes that it is not possible to decide (on these experimental grounds) between 136 and 137 for the above fundamental ratio. W. N. Bond,[5] on the other hand, doubts the validity of Eddington's result and considers that the evidence confirms the classical equation for Rydberg's constant, viz., $R = 1·0968 \times 10^5 = (e^5/h^3)[2\pi^2/c(1 + m/M)(e/m)]$. J. H. J. Poole[6] considers that a larger value of π might hold in the intense electric fields within the atom and might be used for the calculation of $hc/2\pi e^2$. Other speculations on possible integral relations between sub-atomic constants have been put forward by V. Rojansky[7] and by E. E. Witmer.[8] The former suggests that the ratio of the mass of the proton to that of the electron may be $136^2/10 = 1849·6$, the denominator and the square root of the numerator being possible numbers of degrees of freedom in the theory put forward by Eddington. The latter author's suggestion is that this mass ratio should be simply related to an integer and points out that $1849 = 43^2 =$

[3] *Proc. Roy. Soc.*, 1929, [*A*], **122**, 358; *A.*, 231.
[4] *Nature*, 1929, **123**, 409; *A.*, 369; see also R. T. Birge, *ibid.*, p. 318; *A.*, 368.
[5] *Ibid.*, 1929, **124**, 408; *A.*, 1125.   [6] *Ibid.*, 1929, **123**, 530; *A.*, 484.
[7] *Ibid.*, p. 911; *A.*, 861.   [8] *Ibid.*, 1929, **124**, 180; *A.*, 973.

$1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2$ which is half of $(2 + 8 + 8 + 18 + 18 + 32)$ which is the atomic number of the heaviest member of the zero group of elements. R. Fürth [9] points out that this mass ratio is of the same order of magnitude as hc/e^2 and shows that the ratio can be deduced from the quantum and relativity theories. In a later paper [10] he deduces the actual masses of the electron and the proton from the fundamental magnitudes of these theories.

There is now a considerable amount of direct experimental evidence in favour of the de Broglie wave theory of the electron. G. P. Thomson,[11] by using a stream of nearly homogeneous cathode rays from an induction coil in what is practically his father's classical apparatus, has shown that metals such as aluminium, gold, and platinum produce diffraction patterns just as with X-rays, and that their crystal constants, obtained by applying de Broglie's theory, agree to 1% with those determined by X-ray analysis. Similar results have been obtained for celluloid,[12] copper, silver, and tin,[13] and for gold, silver, lead, iron, and nickel,[14] although the last-named gave an unexpected result. Evidence has been obtained that the electrons must be accompanied by a train of not less than 50 waves in length, and it has been shown [15] that the above experimental results may be exactly predicted from an application of the ordinary laws of electrodynamics to the motion of an electron consisting of the usually accepted point charge surrounded by a system made up of parts which can be set in motion by electric forces and, when in motion, produce the effects of electric currents. This system surrounding the nuclear charge will have a definite vibration period, the frequency of which is proportional to the square root of the number of electrified systems per unit of volume, and these vibrations form an oscillating electric field in which there is no transmission of energy. Both the nuclear charge and the surrounding system can vibrate and, in the steady state of the electron, the vibrations are in resonance. The total energy of the electron is that due to the charge on the nucleus together with that due to the oscillating field, a conception which is of importance in connexion with the calculation of the size of the electron. E. Rupp,[16] working along similar experimental lines, has examined the deflexion phenomena which occur when electrons pass through thin

[9] *Naturwiss.*, 1929, **17**, 688; *A.*, 1123.
[10] *Ibid.*, p. 728; *A.*, 1209.
[11] *Proc. Roy. Soc.*, 1928, [*A*], **117**, 600; **119**, 651; *A.*, 1928, 3, 938.
[12] A. Reid, *ibid.*, 1928, [*A*], **119**, 663; *A.*, 1928, 938.
[13] R. Ironside, *ibid.*, p. 668; *A.*, 1928, 938.
[14] *Ibid.*, 1929, [*A*], **125**, 352; *A.*, 1209.
[15] (Sir) J. J. Thomson, *Phil. Mag.*, 1928, [vii], **6**, 1254; *A.*, 231.
[16] *Ann. Physik*, 1929, [v], **1**, 773, 801; *A.*, 619.

metallic sheets.   He finds that with fairly slow-moving electrons, deviations occur from the de Broglie free-space relation, $\lambda = h/mv$, and accounts for these by introducing a refractive index which is greater than unity.   This is ascribed to the existence of a positive inner lattice potential, E_0, corresponding to the relation $\mu = (1 + E_0/V)^{1/2}$, where V is the electron velocity in volts. E_0 varies from 11 to 17 volts, and is positive for all metals, so that μ is greater than unity, decreases towards unity with increasing electron velocity, and for a given velocity is constant for a given lattice.   Rupp's calculations of the effects of refractive index have been the subject of criticism by G. P. Thomson,[17] but since the effects are small, the discrepancies thus brought out are of little moment.   L. H. Germer [18] has obtained, under suitable experimental conditions, diffraction patterns of four distinct types from the electron diffraction from a single crystal of metal.   One of these is due to the space lattice of the bulk, one to the space lattice of the surface metallic layer, a third to that of a monatomic film of adsorbed gas, and the fourth to that of a thicker gas film.

The problem of the diffraction of an electron wave by a line grating, consisting of a periodic distribution of electric or magnetic material, has been worked out by C. G. Darwin,[19] who concludes that no polarisation can occur with pure electric forces or with some magnetic forces.   In the case where electric and magnetic fields occur simultaneously, some polarisation may occur, but the case has not been worked out in detail.   E. Rupp [20] could detect no such effect with certainty, although there was a slight indication that it might have occurred when a beam of electrons of velocity 150 volts was twice reflected from the (111) face of a copper crystal.   C. J. Davisson and L. H. Germer [21] detected no polarisation when an electron beam was twice reflected from nickel crystal faces at bombarding velocities from 10 to 200 volts.

During the past year, the Royal Society held a discussion [22] on the structure of atomic nuclei in which the progress made in the last fifteen years was reviewed.   The problem has been attacked in three ways : (a) by the proof of the existence of isotopes and the accurate determination of their relative masses, (b) by the artificial disintegration of atoms by bombardment with α-particles, and (c) by a study of the wave-lengths of the penetrating γ-rays which

[17] *Phil. Mag.*, 1929, [vii], **6**, 939.
[18] *Z. Physik*, 1929, **54**, 408; *A.*, 620.
[19] *Proc. Roy. Soc.*, 1928, [*A*], **120**, 631; *A.*, 1928, 1300.
[20] *Z. Physik*, 1929, **53**, 548; *A.*, 483.
[21] *Physical Rev.*, 1929, [ii], **33**, 760; *A.*, 736.
[22] *Proc. Roy. Soc.*, 1929, [*A*], **123**, 373; *A.*, 622.

originate in the disintegration of the nucleus. The discovery of new isotopes has been much facilitated by recent work on band spectra [23] which seem to be superior to the mass spectrograph for detecting those occurring in very small quantity, but, as band spectra give only *relative* masses of two isotopes, the two methods are supplementary.

The scattering of α-particles by atoms is that which would be expected from an inverse-square law of force between the particle and the nucleus for all atoms heavier than copper; with lighter atoms, however, the scattering is abnormal and is explained by assuming that the approaching particle polarises the nucleus and thus gives rise to an attractive force varying as the inverse fifth power of the distance. The scattering of α-particles by hydrogen and helium is quite abnormal and indicates that the nuclei of these atoms must be very flat in shape. Scattering experiments show that α-particles cannot penetrate the nucleus of uranium, but the speed of emission of an α-particle from this nucleus shows that penetration should be possible. This difficulty is got over by the new wave mechanics, which allows the α-particle, or rather, the wave train with which it is identified, to leak through the high-potential barrier surrounding the nucleus, and to emerge with the kinetic energy it possessed when inside the barrier. On this view, the radius of the uranium nucleus is about 7×10^{-13} cm., and into this small nuclear volume must be packed 238 protons and 146 electrons. A picture is presented of the building up of atomic nuclei from protons and electrons, with an energy loss of 7 million electron volts per proton, so that to divide a mercury nucleus into its constituent protons and electrons would require an amount of work equal to 1400 million electron volts. But this view cannot be reconciled with the facts of radioactivity, so that it must be supposed that, for the heavier elements, at least, the main structural unit is the α-particle, which must have a greater energy in the nucleus than in the free state. Applying this view to the facts represented by F. W. Aston's packing fraction curve,[24] one gets the following picture—an instantaneous view only—of the nuclei of the various atoms. For the lighter atoms, a highly concentrated and stable nucleus is formed by the binding of protons, electrons, and α-particles, partly by distortional, and partly by magnetic forces. The formation of this nucleus is accompanied by the loss of mass (energy) and so the process continues up to a nucleus with mass 120, which represents the closest packing and maximum loss of mass. Beyond this point, the additional particles are less and less firmly held and the structure becomes less dense towards the outside, until uranium is reached, where the

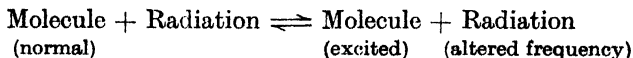[23] See p. 20.   [24] *Ann. Reports*, 1927, **24**, 12.

packing is so loose that the nucleus has as much energy as it can hold. Finally, the whole nucleus is surrounded by a high-potential barrier, which is normally impassable to α-particles (the kinetic energies of which are known) but is occasionally traversed when a particle assumes its alternative wave train identity.

A. C. Burton [25] regards packing fractions in rather a different manner from that preferred by F. W. Aston. He finds the loss in mass due to packing by subtracting the actual mass found from ($1\cdot00778 \times$ mass number) and interprets his results by the help of the rule that, if it is found that in any two cases the addition of the same quantity to the nucleus in passing from one atom to the next produces the same extra loss in mass, it can be concluded that the addition has probably been made in the same way. It is found that the packing is particularly close for atoms of mass $= 4n$. A theory of packing is developed which interprets the existence of Sir E Rutherford's neutrons,[26] and the packing loss due to the loose addition of a neutron is calculated to lie between $0\cdot007$ and $0\cdot008$.

Molecular Structure and Molecular Spectra.

Three types of spectra are now available which may afford evidence of molecular structure : band spectra in the visible and ultra-violet regions, infra-red spectra, and Raman spectra.[27] Of these, the first two are not new, but the study of the last is of comparatively recent development.

The Raman Effect.—This was first noticed as a disturbing effect during the examination of several carefully purified substances for light scattering. The phenomenon took the form of the inclusion in the scattered light of light of altered wave-length. When the incident light was monochromatic, examination of the scattered light revealed its spectral nature, consisting of lines in some cases, more or less diffuse bands in others, and, in addition, a more or less diffuse continuous spectrum accompanying the lines or bands. The Raman effect is closely allied to the Compton effect, and a similar explanation has been advanced ; the following scheme may be used to illustrate it :

$$\text{Molecule} + \text{Radiation} \rightleftharpoons \text{Molecule} + \text{Radiation}$$
$$\text{(normal)} \qquad\qquad\qquad \text{(excited)} \quad \text{(altered frequency)}$$

Thus, if a quantum, $W = hN$, falls on a molecule and alters its energy level from E_1 to E_2, then the energy of the diffused quantum

[25] *Trans. Roy. Soc. Canada*, 1928, [iii], **22**, III, 379; *A*., 372.

[26] *Ann. Reports*, 1927, **24**, 13.

[27] *Trans. Faraday Soc.*, 1929, **25**, 781 ; C. V. Raman, *Indian J. Physics*, 1928, **2**, 387; C. V. Raman and K. S. Krishnan, *ibid*., p. 399 ; *Proc. Roy. Soc.*, 1929, [A], **122**, 23.

is $W' = hN' = hN - (E_2 - E_1)$, and the corresponding frequency $N' = N - (E_2 - E_1)/h = N \pm n$, in which the sign of n depends on whether the energy level of the molecule is raised or lowered. Now E_2 and E_1, and consequently n, are quantities characteristic of the molecule, so that $n = N \sim N'$ is of great interest in studying problems of molecular structure.

In general, of course, when light acts on matter and is re-emitted, the frequency of the radiation is degraded on account of absorption of energy by the matter. This is the meaning of Stokes's law, which is only a particular case of the degradation of luminous frequencies by matter. The Raman effect falls into line with this generalisation, since the secondary negative lines (frequency $N - n$) are more intense than the secondary positive lines (frequency $N + n$).

It is thus possible to classify the interactions between material particles and radiant quanta as follows :

(1) The *photoelectric effect*, where the incident quantum is wholly absorbed : part of it goes to tear an electron out of an atom, and the rest appears as kinetic energy of the electron.

(2) *Fluorescence*, where part of the energy increases the energy level of the molecule, and the rest increases its thermal energy. The first part is re-emitted as a quantum of lower frequency when the molecule returns to its normal state.

(3) The *Compton effect*, where the quantum encounters a free electron at rest, shoots it out with a certain velocity, and is itself re-radiated at a correspondingly lower frequency.

(4) The *Raman effect*, where the quantum encounters a more complicated system (ions, atoms, or molecules) and alters its energy level, being itself re-radiated at a correspondingly different frequency.

The essential difference between fluorescence and the Raman effect is thus that for incident light of frequency N, a molecule with a free period n will emit light of frequency n if it fluoresces and of $N \pm n$ in the Raman effect : a Raman spectrum is essentially an absorption spectrum. Sir C. V. Raman [28] has summarised the characteristic features of the phenomenon as : (a) its universality— it is observed in gases, vapours, liquids, crystals, and glasses; (b) its spectral character; (c) the theoretical explanation, as involving an exchange of energy between the quantum and the molecule, the identification of the frequency difference with a characteristic frequency of the molecule and the consequent utility of the phenomenon as an aid to the exploration of molecular spectra, especially in the infra-red ; (d) the possibility of an increase as well as a decrease of frequency, but the greater probability of the latter; (e) the strong polarisation of the re-emitted radiations; (f) the distinctness

[28] J. Cabannes, *Trans. Faraday Soc.*, 1929, **25**, 800.

of the new phenomenon from fluorescence, but its obvious relation to it; (g) its relation to the Compton effect; and (h) the incoherent nature of the radiation.

In the earlier work on the Raman effect, light from a lamp was focused on to the centre of a bulb containing the liquid under examination and the scattered light was viewed from the side. R. W. Wood,[29] however, has indicated methods of excitation which are much less wasteful of light. The method advocated is to place the liquid in a long tube illuminated from the side by a mercury arc with a cylindrical reflector, or by means of a helium tube wound in a close spiral round the tube. Water-cooling may be necessary, and a careful choice of the exciting lamp is essential, since the Raman radiations are very faint and may be obscured by light scattered in the classical manner if the exciting source emits anything in the nature of a continuous spectrum. Suitable filters may, if necessary, be employed.

It is, of course, impossible in this Report to mention more than a very few of the results which have already been obtained in this direction, but the following selection notes some of the more interesting. All Raman frequencies (positive or negative) characterised by the same change of frequency, $\pm n$, are in the same state of polarisation whatever the frequency, N, of the exciting radiation, but the state of polarisation varies within wide limits.[30] The Raman effect can be observed with powders as well as with clear crystals,[31] and with naphthalene, for example, the effect is the same whether the substance is solid, molten, or dissolved, although there is a difference between the spectrum of the solid and that of the solution in the case of compounds such as sodium nitrate.[32] The Raman spectrum of liquid hydrogen [33] indicates that this substance is a mixture of two effectively distinct sets of molecules in the proportion 2 or 3 to 1, in agreement with the result already obtained from measurements of the specific heat of hydrogen gas.[34] One of the most useful of the features of the Raman effect is that the frequencies of the scattered radiation indicate the existence of vibrations in molecules which are optically inactive or obscure in absorption. Gaps in infra-red spectra had already been inferred : in calcite, for instance, one such missing fundamental has been postulated with a wave-length of 9 μ, and it is precisely this one which shows up very strongly in Raman photographs.[35] In many cases, it is possible to

[29] Trans. Faraday Soc., 1929, 25, 792.   [30] J. Cabannes, ibid., p. 813.
[31] A. C. Menzies, ibid., p. 836.   [32] Ibid., p. 838.
[33] J. C. McLennan, ibid., p. 797.
[34] D. M. Dennison, Proc. Roy. Soc., 1927, [A], 115, 483.
[35] C. Schaefer, Trans. Faraday Soc., 1929, 25, 841.

identify particular frequencies with the vibration of certain chemical bonds in the molecule. For example, the frequency corresponding to the C–H bond is different in aliphatic and in aromatic compounds, and the degree of polarisation strikingly so; [27] benzene shows both types of bond; [36] other links have their characteristic frequencies,[37] and analogy between spectra is more noticeable in homology than in isomerism.[38] Rise of temperature has the effect of diffusing certain Raman lines and it is supposed that this is due to the increase of molecular rotation.[39] The effect is most noticeable in close doublets. Since the frequencies concerned in the Raman effect are the vibration frequencies connected with the return of the molecule from an excited state to its normal electronic level, they should, as has already been pointed out, occur as end states in fluorescence. This has been confirmed for benzene.[40]

Band Spectra.—The new theory of wave mechanics has cleared up many of the complexities of molecular spectra and has led to results of very great importance both to the chemist and to the physicist. Unfortunately, the nomenclature is so complex, and the results are so detailed, that it is not possible to give an account of this work here. A few only of the results can be mentioned and, for the rest, the reader is referred to the Report of the Symposium of Molecular Structure and Molecular Spectra held by the Faraday Society at Bristol on September 24th and 25th, 1929,[41] which contains 40 papers and reports and 3 discussions. A further account, as far as work in the infra-red is concerned, is to be found in " Infra-Red Analysis of Molecular Structure " by F. I. G. Rawlins and A. M. Taylor [42] which has recently appeared.

The inhomogeneity of hydrogen, to which reference has already been made,[43] has been deduced from considerations of the alternating intensities of lines in band spectra as accounted for by nuclear spin.[44] Calculations show that, owing to minute perturbations between the nuclei, interchange between the two forms of hydrogen is complete in about a month, so that hydrogen, though a mixture, does not consist of two sets of independent components. At absolute zero, there is no rotation, so that all molecules must then be identical.

[36] A. Dadieu and K. W. F. Kohlrausch, *Physikal. Z.*, 1929, **30**, 384; *A.*, 976.
[37] A. Petrikaln, *Z. physikal. Chem.*, 1929, [*B*], **3**, 360; *A.*, 865.
[38] A. Dadieu and K. W. F. Kohlrausch, *Naturwiss.*, 1929, **17**, 366; *A.*, 866.
[39] Y. Fujioka, *Nature*, 1929, **124**, 11; *A.*, 976; *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, **11**, 205; *A.*, 1361.
[40] C. V. Shapiro, *Nature*, 1929, **124**, 372; *A.*, 1127.
[41] *Trans. Faraday Soc.*, 1929, **25**, 611—949.
[42] Cambridge University Press.
[43] See p. 18.
[44] R. S. Mulliken, *Trans. Faraday Soc.*, 1929, **25**, 634.

If, therefore, hydrogen is kept at a very low temperature for a sufficient length of time, it should become more homogeneous and thus have a different specific heat from that of ordinary hydrogen. This experiment has been made with success.[45]

Thermal-conductivity measurements at low pressures show that the transformation of ordinary (mixed) hydrogen into the para-form is incomplete even after a year, but at high pressures (350 atm.) at the temperature of liquid air, practically the theoretical quantity of para-hydrogen can be obtained in a week. Para-hydrogen is fairly stable for a week at the ordinary temperature in glass vessels, whilst at 100 atm. it slowly reverts to ordinary hydrogen in metal vessels, but in the presence of platinised asbestos the change occurs at once. Adsorption on charcoal at the temperature of liquid air gives practically pure para-hydrogen. The pure para-form has a vapour pressure of 787 ± 1 mm. at $20 \cdot 39°$ K., the temperature at which the ordinary form boils. Its melting point is $13 \cdot 83°$ K., as against $13 \cdot 96°$ K. for the ordinary form.

The spectrum of nitrogen presents difficulties.[46]

Since the various band spectra constants depend on the mass of the vibrating nucleus, it follows that band spectra should be of use in detecting the presence of isotopes. Recent work on this subject has been summarised by R. T. Birge,[47] and it may be stated that the existence of mass 17 [48] and mass 18 [49] isotopes of oxygen and a mass 13 isotope of carbon [50] is now definitely established. It may be, therefore, that all elements have isotopes, although the agreement of F. W. Aston's mass determinations with atomic weights as determined by chemical means proves that any isotopes as yet undetected must occur in very small quantity indeed.

A problem of the greatest importance to the chemist is that of molecular formation and dissociation. The first part of the problem has been considered by F. London,[51] alone and in collaboration with W. Heitler.[52] The application of the theory of spectra gives results which also follow qualitatively from the well-known theory of valency of G. N. Lewis, but the new point of view has wider possibilities on account of its quantitative nature. The second part of

[45] K. F. Bonhoeffer and P. Harteck, *Naturwiss.*, 1929, 17, 182, 321; *A.*, 479; *Z. physikal. Chem.*, 1929, [B], 4, 113; *A.*, 982.

[46] F. Rasetti, *Nature*, 1929, 123, 757; *Physical Rev.*, 1929, 34, 367; *Proc. Nat. Acad. Sci.*, 1929, 15, 515.

[47] *Trans. Faraday Soc.*, 1929, 25, 719.

[48] W. F. Giauque and H. L. Johnston, *Nature*, 1929, 123, 318; *J. Amer. Chem. Soc.*, 1929, 51, 1436.

[49] *Idem, Nature*, 1929, 123, 831.

[50] A. S. King and R. T. Birge, *ibid.*, 1929, 124, 127; R. T. Birge, *ibid.*, p. 182.

[51] *Z. Physik*, 1928, 50, 24.   [52] *Ibid.*, 1927, 44, 455.

the problem was first attacked from the standpoint of the theory of spectra three years ago [53] and an improved method has now been suggested.[54] It has been observed that sets of vibrational levels in a molecule often converge to a limit, *i.e.*, the separation of successive levels becomes smaller and smaller towards zero, and it is considered that this limiting point represents dissociation of the molecule. When the series can be followed up to, or nearly to, the point of convergence, the heat of dissociation can then be deduced when the energy content of the dissociated atoms is known. When, however, an incomplete set of levels only can be obtained, the method of extrapolation referred to above may be employed. It leads to values of the heats of dissociation of nitrogen and oxygen which agree well with the accepted value for the heat of dissociation of nitric oxide, and in other bands [55] the method has given values for the heats of dissociation of C–H and N–H groups in good agreement with thermal data.

Tesla-luminescence Spectra.—Further results of investigations on this subject have appeared since it was last mentioned in these Reports.[56] Many substances of varied chemical type have been examined,[57] and up to the present it has been found that the only groups capable of forming centres of emission under the Tesla discharge are the benzene ring and the carbonyl radical. The benzene ring gives a banded spectrum in the ultra-violet, which is modified by substituent groups, sometimes in a very marked manner, so that occasionally the ultra-violet spectrum is completely suppressed and replaced by a glow or a banded spectrum in the visible region : sometimes, again, both visible and ultra-violet spectra are observed.[58] The aliphatic aldehydes and ketones emit a continuous spectrum, without bands, in the blue region, and those aromatic aldehydes which give the Tesla effect emit a banded spectrum in the same region but do not show the characteristic benzene spectrum.[59] More careful examination [60] of some compounds which had previously been reported as not giving Tesla spectra has shown that they do, in fact, show faint emission. " In all the banded spectra obtained, it has been found that a simple wave-number relationship holds between the bands, the series of

[53] R. T. Birge and (Miss) H. Sponer, *Physical Rev.*, 1926, **28**, 259; *A.*, 1926, 993.

[54] R. T. Birge, *Trans. Faraday Soc.*, 1929, **25**, 707.

[55] J. W. Ellis, *ibid.*, p. 888.   [56] *Ann. Reports*, 1923, **20**, 9.

[57] W. H. McVicker, J. K. Marsh, and A. W. Stewart, *J.*, 1924, **125**, 1743; 1925, **127**, 999.

[58] J. C. Macmaster, A. Russell, and A. W. Stewart, *J.*, 1929, 2401.

[59] A. Russell and A. W. Stewart, *ibid.*, p. 2407.

[60] *Idem, ibid.*, p. 2432.

bands, for any one compound, being divisible into groups, the members of which exhibit a constant difference from their congeners in other groups." Benzene and its simple substitution products have been found to emit identical spectra when their vapours are excited either by the Tesla discharge or by the short waves from a mercury lamp.[61]

The Mesomorphic States (Mesophases or Liquid Crystals).

It is now generally recognised that " liquid crystals " are phases intermediate between the crystalline (solid) and amorphous (liquid) states. G. Friedel [62] considers that there may be two or possibly more such mesophases between the true crystal and the true liquid so that the order of succession of phases is always : Crystalline, smectic (soap-like), nematic (thread-like), liquid, with increasing temperature or increasing dilution. It is very well known that mesophases are exhibited only by molecules which are long and unbranched, and it appears that, in most cases, one of the meso-morphic states is not exhibited. When, however, they both appear, they invariably do so in the above order. This limitation of the phenomenon to substances which possess long molecules is supported by the observation of W. H. Martin,[63] who finds that the depolaris-ation factor of the light scattered by dust-free p-azoxyanisole is 0·85 : the calculated value for a liquid composed of molecules which can vibrate only in one direction is 0·86. The transition from one phase or mesophase to the other is always perfectly definite and appears in every case to conform strictly to the phase rule. That is to say, in a one-component condensed system the transition is governed by temperature only, in a two-component system, by the temperature and the composition, and so on. Excellent examples of these transitions may be found in the work on soap of J. W. McBain and his colleagues,[64] who call the crystalline phase the " curd," the smectic phase the " neat soap," and the nematic phase the " middle soap."

The smectic phase may exhibit a plane homogeneous or a conic structure : it is birefringent and always positively uniaxial. The molecular elements making up the structure are arranged with their long axes parallel, but are turned around this direction in a random manner. X-Ray analysis has shown that the smectic structure

[61] J. K. Marsh, J., 1923, **123**, 820, 3315; (Miss) M. W. Monypeny and A. Russell, J., 1929, 2436.

[62] Ann. Physique, 1922, [ix], **18**, 273; A., 1923, ii, 223.

[63] Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 36; A., 1926, 15.

[64] J. W. McBain and A. J. Burnett, J., 1922, **121**, 1320; J. W. McBain and G. M. Langdon, J., 1925, **127**, 852; J. W. McBain and W. J. Elford, J., 1926, 421.

consists of parallel planes at equidistant intervals, and the direction perpendicular to these planes is the only one in which the periodicity of the crystal is imitated—in the case of sodium oleate,[65] for example, the distance between the smectic planes has been found by X-ray analysis to be 43·5 Å., confirming previous measurements on soap bubbles. A magnetic field has no effect on molecular orientation in the smectic state (but see below).

The nematic state is divided into two types, the true nematic and the cholesteric. The former is birefringent and positively uniaxial. It shows no sign of parallel plane structure, but exhibits a thread-like structure corresponding to the conic structure of the smectic state. The optic axis alines itself parallel to a magnetic field and perpendicular to an electric field. The cholesteric state, however, differs from the others in being always negatively uniaxial. It is invariably associated with rotatory power and may be assumed either by an optically active compound or by a mixture of an optically active substance with a compound in the true nematic state. Thus, whilst there is a sharp discontinuity between the smectic and either of the nematic states, the true nematic state may merge continuously into the cholesteric. A substance in the cholesteric state may resemble a smectic phase in appearance, showing both plane and conic forms. Substances in the plane form of the cholesteric state may show enormous rotatory powers up to 140,000° per mm. and this has no relation to the rotatory power of the substance in the molten or dissolved state.

We may thus picture the gradual transition of matter by the action of thermal or solvent forces from the crystal form, with its ordered arrangement of planes in three or more directions, by a sudden jump to the smectic state with somewhat less order, having its planes ordered in one direction only. A second jump leads to the nematic state, where the only trace of order remaining is the parallel orientation of the molecules. A final jump leads to the amorphous or liquid state of molecular chaos.

H. Zocher and V. Birstein [66] have recently published accounts of experiments on mesophases which in the main confirm G. Friedel's views and observations. In the nematic and the smectic state, differences in surface tension are responsible for the orientation of the elements to the bounding surface. In some cases slight changes in the condition of the surface profoundly modify the orientation of the phase : e.g., an acid-treated glass surface induces p-azoxyanisole to set itself perpendicular to the surface, whereas an alkali-treated

[65] M. de Broglie and E. Friedel, *Compt. rend.*, 1923, **176**, 738.

[66] *Z. physikal. Chem.*, 1929, **141**, 413; **142**, 113, 126, 177, 186; *A.*, 870, 876, 1013; see also H. Zocher, *Physikal. Z.*, 1927, **28**, 790; *A.*, 1928, 226.

surface induces parallel orientation. The aqueous mesophase of salvarsan is nematic, and addition of sucrose or dextrose gives rise to the twisted structure and rotatory power characteristic of the conversion of the nematic to the cholesteric state, although the twisted structure may often be observed when such optically active substances have not been added : when this is the case, however, the direction of the twist is right or left indifferently.

Of the oleates, palmitates, and stearates of sodium and potassium, only the first show aqueous mesophases, and ammonium oleate solutions prepared from concentrated ammonia and oleic acid give no evidence of an aqueous mesophase. Both sodium naphthenate and cetyl xanthate form a smectic mesophase in aqueous solution, and the birefractive dispersion of the latter is anomalous. G. Friedel has previously stated that 10-bromophenanthrene-6-sulphonic acid formed anhydrous crystals which passed into the smectic state on the addition of water, to the nematic state on further dilution, and finally to an ordinary solution on still further dilution, all at laboratory temperature. These results are now confirmed and the additional observation is made that the nematic phase which is formed at moderate concentrations shows, in contrast to the nematic mesophases already known, a negative stream double refraction and forms drops with optically positive radii. It is noteworthy that commercial lecithin forms a mesophase, whils synthetic lecithin does not.

For compounds, such as p-azoxyanisole, which have a symmetrical molecular structure, the dielectric and the magnetic anisotropy of the nematic phase are negative, but when the structure is asymmetric, both the dielectric and the magnetic anisotropy are positive. By the use of strong electric fields of the order of 10,000 volts per cm., it is shown that, contrary to Friedel's statement,[67] cholesteric phases such as that of optically active amyl ethoxybenzylideneamino-α-methylcinnamate are oriented and become doubly refracting. The optical activity is considerably diminished by the field, but removal of the field destroys the birefringence and restores the normal optical activity. Smectic mesophases are also influenced by electric fields of sufficient strength. In all the cases studied, the magnetic anisotropy is positive and the dielectric anisotropy negative, even when that of the corresponding nematic phase is positive.

A new type of sol having many of the properties of a mesophase has been described by H. Zocher and K. Jacobsohn.[68] These authors have given the name " tactosol " to sols containing non-spherical particles which have the property of spontaneously

[67] G. Friedel, *Ann. Physique*, 1922, [ix], **18**, 273; *A.*, 1923, ii, 223.
[68] *Kolloidchem. Beih.*, 1929, **28**, 167; *A.*, **505**.

arranging themselves in parallel order. Vanadium pentoxide, benzopurpurin, ferric oxide, tungsten trioxide, and chrysophenin have been found to form tactosols. Vanadium pentoxide, on ageing, separates into a concentrated anisotropic phase—the tactosol—which later is precipitated, and a dilute isotropic phase, which is termed the " atactosol." The process is greatly retarded by the addition of arsenic acid, whilst the addition of other electrolytes does not affect the ageing, although it affects the closeness of packing of the particles. The application of an electric potential difference causes the particles to arrange themselves with their long axes parallel to the direction of the current, but an alternating current has the effect of orienting the particles perpendicular to its direction. In a magnetic field, the particles are arranged parallel to the lines of force. Tactosols are readily produced by cooling a 2% boiling sol of benzopurpurin-4B, or a 1% sol of benzopurpurin-6B. Electrolytes have the same effect on this tactosol as on that of vanadium pentoxide, but a magnetic field causes the particles to arrange themselves with their long axes perpendicular to the lines of force. Tactosols of tungsten trioxide have disc-like, negatively charged particles which consist of a number of parallel platelets having a constant period or distance apart. This period is diminished by increasing the electrolyte content of the sol.

Intensive Drying.

The problem of intensive drying is still the subject of much controversy. Many workers assert that the properties of substances are altered by intensive drying and they favour, in general, the explanation [69] that such change in properties is the result of the retardation or even the complete prevention thereby of the establishment of the inner equilibrium which is normally rapidly attained between different molecular species in chemically pure substances. Other workers, however, deny that intensive drying causes any change of properties, and the experimental evidence for their attitude falls into two classes. On the one hand, there are investigators who have completely failed to observe any change of properties of substances after intensive drying, and on the other, there are critics who state that some, at least, of the changes which are said to be produced by intensive drying can be observed with material which has not been dried at all.

H. B. Baker [70] has measured the vapour densities of numerous substances after intensive drying for periods varying from 2 to 15 years, and finds increases in the molecular complexity in all cases. A diminution of about 30% in the latent heat of vaporisation of

[69] *Ann. Reports,* 1927, **24,** 21.   [70] J., 1928, 1051.

benzene after $3\frac{1}{2}$ years' drying was also observed. This worker favours the hypothesis [71] that the action of water in promoting molecular dissociation is due to its high dielectric constant and, in support of this view, adduces the experimental fact that benzene, hexane, and carbon disulphide, when not intensively dried, have their boiling points raised by application of a voltage of 400 to platinum plates immersed in them. A. Smits [72] attributed this effect, in part at least, to superheating, and on repeating the experiment and determining vapour pressures, failed completely to observe any alteration produced by the electric field. This worker concludes that large effects after intensive drying are to be expected in rapid-distillation experiments, but small or zero effects in vapour-pressure measurements. He regards surface-tension measurements as untrustworthy criteria of molecular complexity, since the magnitude of this property may be altered by the removal of dust particles from a liquid during long standing. On reviewing the available evidence, he concludes that the inner equilibria of solids and gases have been fixed by the treatment under discussion, but that, in the case of liquids, the inner transformations have been retarded but not absolutely stopped. Drying by means of low temperatures has been employed [73] for various gases, but this process appears, in general, to be ineffective in preventing chemical action or in altering the boiling point of ether. The duration of contact with phosphoric oxide necessary to realise the utmost drying is not more than 6 months according to the experiments of W. A. Bone, F. R. Weston, and D. A. Winter [74] with carbon monoxide and oxygen. J. J. Manley,[75] as a result of measurements of the refractive index of benzene in contact with phosphoric oxide for varying periods of time, infers that water is removed in two stages, the first part to be removed being that which is mechanically admixed, and the last, that which is chemically combined.

The effect of intensive drying on the reduction of metals by hydrogen and by carbon monoxide [76] has been investigated. No effect was observed with silver and mercury oxides and carbon monoxide or with copper oxide and hydrogen, but the temperature required to effect reduction of copper and bismuth oxides by means of carbon monoxide was raised. H. L. Riley [77] has failed to observe any change in the dielectric constant of oxygen after intensive drying.

[71] (Sir) J. J. Thomson, *Phil. Mag.*, 1893, **36**, 320.   [72] *J.*, 1928, 2399.

[73] D. McIntosh, *Proc. Nova Scotian Inst. Sci.*, 1928, **17**, 142; *A.*, 271.

[74] *Proc. Roy. Soc.*, 1929, [*A*], **123**, 285; *A.*, 515.

[75] *Nature*, 1929, **123**, 907; *A.*, 753.

[76] R. H. Purcell, *J.*, 1928, 1207.   [77] *Ibid.*, 1929, 1026.

J. Timmermans [78] found no change in the freezing points and surface tensions of benzene, *p*-xylene, and *cyclo*hexane after 35 months' intensive drying, and similar negative results on the boiling points of benzene and carbon tetrachloride after 4 years' drying are reported.[79] A series of very careful experiments has been carried out [80] on the density and surface-tension changes occurring when benzene is intensively dried, measurements being made on the bulk of the liquid and on middle, head, and tail fractions. The density changes observed were not more than 7 parts in 100,000 parts, and the surface-tension changes were smaller and in the opposite sense to those previously recorded by H. B. Baker.[81] These authors " still feel it to be inconceivable that any considerable molecular association or dissociation could occur in a liquid without causing readily measurable changes in density as well as in surface tension. . . . Though material changes may yet occur, the conclusion at this stage is, evidently, that intensive drying has not produced any change in the density or surface tension of benzene such as would justify an assumption of appreciable change in degree of association or of fractional separation of pseudo-components."

H. B. Baker's reply [82] to those who fail to repeat his observations is that intensive drying manipulation is full of pitfalls for the unwary. Great care is needed in the selection of the glass, to avoid capillaries in the walls of the apparatus which may fill with water, in cleaning, in drying, in the selection of a lubricant, and in the purification of materials. Neglect to observe any one of the many precautions detailed in this paper may lead to failure. W. A. Bone [83] has published a similar note on the precautions to be observed in drying gaseous media.

S. Lenher [84] states that the elevation of the boiling points of liquids which have not been intensively dried can be readily observed when the heating is carried out in a bath, and that the phenomenon is entirely one of superheating. Benzene was superheated by 10° and, when freed from dust,[85] the liquid temperature was raised to 106° before boiling occurred. Carbon tetrachloride was superheated by 30° and water by 12°. He considers that the appearance of bubbles in a liquid is not evidence that the liquid is at its boiling

[78] *Bull. Soc. chim. Belg.*, 1929, **38**, 160.; *A.*, 991.

[79] S. Lenher and F. Daniels, *Proc. Nat. Acad. Sci.*, 1928, **14**, 606; *A.*, 1928, 1189.

[80] H. V. A. Briscoe, J. B. Peel, and P. L. Robinson, *J.*, 1929, **368**.

[81] *J.*, 1922, **121**, 563.

[82] *J.*, 1929, 1661.

[83] *Ibid.*, p. 1664.

[84] *Nature*, 1929, **123**, 907; *A.*, 872; *J. Physical Chem.*, 1929, **33**, 1579.

[85] See also J. W. Smith, *ibid.*, p. 788.

point and insists that vapour pressure is the only admissible criterion. He further points out that the failure of a refluxing drop to coalesce with the bulk of the liquid may quite well be due to a difference of surface tension caused by a difference of temperature rather than to a difference of surface tension caused by a variation of composition. All who have observed this phenomenon on a briefer scale in an ordinary laboratory distillation will be inclined to agree. In another paper [86] he points out that he observed no elevation in the boiling point of intensively dried liquids heated electrically by means of a wire in the liquid and not in a bath. W. A. West and A. W. C. Menzies [87] have conducted experiments on the effect of prolonged heating on the vapour pressures of liquids. They were unable to observe any lag in the return to the normal value on cooling in the cases of benzene, water, acetone, ether, and acetic acid, and found only a small lag in the case of sulphur, which they ascribe to difficulty in establishing thermal equilibrium. They made the interesting observation on acetic acid, which they found to retain water tenaciously even after very close fractionation, that when heated it evolves a more volatile fraction, which presumably contains a larger proportion of water. On cooling, this fraction condenses last and remains for an appreciable time on the surface of the bulk of the liquid, and hence gives rise to a higher vapour pressure. After the liquid has stood for a time, or immediately after it has been shaken, the vapour pressure returns to its normal value. These authors consider that this observation may explain some of H. B. Baker's results. A. Smits has repeated, with variations, his experiments on the vapour pressure of intensively dried n-hexane,[88] and has concluded that further work is necessary if convincing results are to be obtained.[89] In the same paper, he records results which show that his previously reported increase of the vapour pressure of nitrogen tetroxide [90] does not necessarily indicate a shift of the inner equilibrium, but may be due to the evolution of nitrogen tetroxide and oxygen by the action of nitric acid (dissolved in the nitrogen tetroxide used for the experiment) on the phosphorus pentoxide. It is found that 5 years' intensive drying of ammonia has no effect on its melting point. Another paper [91] contains a description of a method for removing gases completely from volatile substances prior to vapour-pressure measurements.

[86] *Proc. Nat. Acad. Sci.*, 1928, **14**, 606.
[87] *J. Physical Chem.*, 1929, **33**, 1893.   [88] *J.*, 1927, **949**.
[89] A. Smits, E. Swart, and P. Bruin, *J.*, 1929, 2712.
[90] A. Smits, W. de Liefde, E. Swart, and A. Claassen, *J.*, 1926, 2657; see also *Ann. Reports*, 1927, **24**, 20.   [91] A. Smits and E. Swart, *J.*, 1929, 2724.

Periodic Precipitates.

A considerable amount of work has been done on the conditions of formation of periodic precipitates or Liesegang rings. M. Copisarow [92] has shown that, for their formation, the salt–salt or salt–acid systems may be replaced by a base, e.g., sodium carbonate, caustic soda, baryta, etc., and a gas or its aqueous solution, e.g., hydrogen chloride, formaldehyde, or ammonia. The presence of a gel is not necessary for the formation of these rings, since they may be formed in purely aqueous solution, as when a solution of sodium carbonate is carefully run over a solution of calcium chloride. A similar observation with calcium hydroxide has been made by W. M. Fischer and A. Schmidt.[93] In this case, another phenomenon may also be observed, viz., the formation of trees and streamers. This formation is inhibited in the presence of gelatin or agar-agar, and both phenomena are greatly influenced by temperature. Light has a directive influence on tree formation, as in more than 70% of the cases the trees spiralled towards the illuminated side of the vessel. When rings were formed in a vessel illuminated on one side, they seemed invariably to incline towards that side. He concludes that rings and trees are special cases of the Liesegang phenomenon, the former being produced under very mild conditions and the latter under the influence of forced irregular diffusion. Furthermore, the primary cause of the phenomenon is the periodic deformation or systematic orientation of a mobile medium which may be either a colloid or finely divided suspended matter. The whole aspect of the phenomenon is therefore widened and earlier theories are inadequate to account for it. P. B. Ganguly [94] has obtained mother-of-pearl-like deposits from an aqueous solution of calcium hydrogen carbonate containing gelatin, and finds that for each concentration of the salt there is a definite range of gelatin concentrations which yield these deposits. N. R. Dhar and A. C. Chatterji [95] conclude from conductivity and diffusion measurements that salts such as silver chromate and lead iodide in gelatin are present as peptised sols and not as supersaturated solutions. They, too, conclude that earlier theories are inadequate.

Periodic precipitates in the absence of jellies have also been obtained [96] by suspending capillary tubes containing calcium chloride solution with their open ends dipping in a saturated solution of sodium phosphate. Banded precipitates were also obtained with

[92] J., 1927, 222.
[93] Rocz. Chem., 1926, 5, 404; A., 1927, 199.   [94] J., 1926, 1381.
[95] Z. anorg. Chem., 1926, 159, 129; A., 1927, 200.
[96] R. J. Doyle and H. Ryan, Proc. Roy. Irish Acad., 1929, 38, [B], 435; A., 1144.

lead nitrate and potassium iodide in the absence of gels, and it was found that the distances between successive bands were in geometrical progression and that the distance of any band from the origin was proportional to the square root of the time taken for its formation.   It was also shown that the formation of the bands takes place, not at the head of the diffusion wave, but behind it.   The complexity of a Liesegang ring formation has been pointed out by M. S. Dunin and F. M. Schemjakin,[97] who have carried out diffusion experiments in tubes 150 cm. long, left in the dark for 18 months. The resultant structures (of silver chromate, silver phosphate, and lead iodide) showed three definite periods, a large-scale periodicity, the ordinary rings, and microscopic rings between the ordinary rings.   It is suggested that the precipitations are controlled by three critical concentrations.

E. S. Hedges and (Miss) R. V. Henley [98] have studied the formation of banded precipitates of silver dichromate and of magnesium hydroxide in gelatin and of lead iodide in agar-agar.   In each case, by mixing equivalent quantities of the reactants in the gel, and then superimposing a strong solution of the diffusing electrolyte, it was possible to separate the chemical reaction from the formation of precipitate.   Since rings were obtained in these experiments comparable with those formed by chemical reaction, it follows that the formation of periodic structures is a coagulation phenomenon taking place after the chemical reaction, so that periodic structures are to be distinguished from periodic reactions.   Periodic structures were also obtained by the diffusion of an electrolyte other than one of the reactants.   The relative amounts of product in the bands and in the clear spaces were determined for a magnesium hydroxide gel (produced from magnesium chloride and ammonia) by chemical analysis. The ratio of magnesium hydroxide in the band to that in the clear space was about 12 to 1, and the corresponding ratio for the ammonium chloride about 1 to 3.   J. R. I. Hepburn [99] points out that the work of Hedges and Henley supports the coagulation theory of Freundlich,[1] and cites some interesting observations on the production of rings of basic copper carbonate by their method. With sodium carbonate as the diffusing electrolyte the colour of the rings was violet, but with copper sulphate only a single green ring was obtained.   Alternate blue and green bands of copper hydroxide have also been described.[2]   The activity product of the ions of magnesium hydroxide in a banded gel has been measured [3] and

[97] *Kolloid-Z.*, 1929, **48**, 167; *A.*, 879.   [98] *J.*, 1928, 2714.   [99] *J.*, 1929, 213.

[1] " Colloid and Capillary Chemistry," p. 735.

[2]. D. Namasivayam, *J. Proc. Asiatic Soc. Bengal*, 1924, **20**, 367; *A.*, 1927, 199.

[3] R. Fricke and O. Suwelack, *Z. physikal. Chem.*, 1926, **124**, 359; *A.*, 1927, 310.

found to increase for some distance beyond the last precipitate and then to fall again. It is concluded that the phenomenon is due to the ordinary processes of diffusion and precipitation, and is not peculiar to solutions containing substances in the colloidal state. Periodic precipitates have also been observed with sulphides,[4] antigen and antiserum,[5] and gold and platinum.[6] B. Kisch [7] makes the interesting observation that the width of Liesegang rings can be modified by means of an electric field. With silver nitrate diffusing into dichromate in gelatin, diffusion occurs more rapidly and the rings are broader and more strongly marked in the direction of the cathode.

The formation of a periodic precipitate has recently been demonstrated by E. S. Hedges [8] in a reaction of the simplest possible character. Concentrated aqueous hydrogen chloride was allowed to diffuse into concentrated aqueous sodium chloride and bands of sodium chloride increasing in thickness and distance apart were obtained. Thus the chief features of the Liesegang phenomenon have been duplicated as a result of a reaction involving no gel, and only two diffusible products. Since, moreover, the bands were composed of relatively large crystals, adsorption effects must have been negligible; these results, therefore, are directly at variance with most of the theories of the formation of Liesegang rings.

The Parachor.

Work on the parachor has been considerably extended since the last mention of this subject in these Reports.[9] The value of the parachor constant for the semipolar double bond has been confirmed, and the method applied to a determination of the structural formulæ of some cyclic sulphones.[10] It has also been used [11] in a successful attempt to confirm the conclusions of C. K. Ingold and C. W. Shoppee [12] with regard to ring-chain valency tautomerism in some derivatives of phorone. As a result of the work of S. Sugden and his colleagues, the periodic table of parachors is rapidly filling up. In the first short period [13] there is a sharp minimum in the atomic parachor at carbon, just as there is in the atomic volume in

[4] S. M. Kuzmenko, *Ukraine Chem. J.*, 1928, **3**, 231; *A.*, 1928, 1187.

[5] L. Reiner and H. Kopp, *Kolloid-Z.*, 1927, **42**, 335; *A.*, 1927, 932.

[6] E. C. H. Davies and V. Sivertz, *J. Physical Chem.*, 1926, **30**, 1467; *A.*, 1927, 18.

[7] *Kolloid-Z.*, 1929, **49**, 154; *A.*, 1382.

[8] *J.*, 1929, 2779.   [9] *Ann. Reports*, 1927, **24**, 15.

[10] A. Freiman and S. Sugden, *J.*, 1928, 263.

[11] S. Sugden, *ibid.*, p. 410.

[12] *Ibid.*, p. 365.   [13] J. J. Etridge and S. Sugden, *ibid.*, p. 989.

the solid state.   It is also found [14] that there is a regular distribution in the atomic parachors along the periods and down the groups of the periodic table.   The parachor for a semipolar double bond is, as would be expected, identical with that for the polar bond in fused salts.[15]

The hypothesis of singlet bonds is of great service in accounting for the parachors of the higher halides and co-ordinated compounds of uni-, bi-, and ter-valent metals.[16]   Postulation of duplet bonds in these compounds leads to sizes of the electron shells about the central atoms which bear no simple relation to the observed parachor anomalies unless it is assumed that the sharing of an electron brings about a diminution of about 12 units in the parachor.   Now, in deducing parachor constants, the contribution of a single bond is assumed to be zero, i.e., the sharing of an electron is assumed to have no effect.   Since atomic parachors have been calculated from measurements on compounds in which the constituent atoms exert their normal valencies, this assumption will have no effect when these values are used to predict the parachors of other normal compounds : any error is automatically compensated.   The same compensation is found for compounds containing semipolar double bonds.   For higher halides (such as phosphorus pentachloride) and co-ordinated compounds, however, this compensation does not occur, and the observed values of the parachors can be accounted for equally well by the hypothesis of singlet bonds, or by assuming that duplet bonds exist between the atoms and that sharing gives a contraction of 12 units per electron.   A direct test which distinguishes between these hypotheses is provided by data on elementary mercury and mercury diphenyl and on two thallium compounds.   The experimental figures show that electron sharing has little or no effect on the parachor.   Other workers have shown [17] that compounds of quadrivalent selenium differ characteristically from similar compounds of sulphur : sulphoxides are readily oxidised to sulphones, but the corresponding selenoxides cannot be similarly oxidised ; furthermore, unsymmetrical sulphoxides of the type $R_1R_2S \Longrightarrow O$ have been resolved into enantiomorphous forms, but the corresponding selenoxides have resisted all attempts at resolution.   It therefore seemed possible that the octet rule might not hold for selenium.   The results of parachor measurements lend no support to this view.   S. Sugden has compared the zero volumes, parachors,

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[14] W. J. R. Henley and S. Sugden, *J.*, 1929, 1058, and other papers of this series.

[15] S. Sugden and H. Wilkins, *ibid.*, p. 1291.   [16] S. Sugden, *ibid.*, p. 316.

[17] W. R. Gaythwaite, J. Kenyon, and H. Phillips, *J.*, 1928, 2280, 2287; *idem* and O. K. Edwards, *ibid.*, p. 2293.

and critical volumes of some gaseous elements and compounds with the diameters of their molecules as calculated from viscosity data.[18] It is found that the parachor conforms more closely to the requirements of an ideal additive function than any of the other properties.

The determination of the parachors of substances in solution has been studied by D. L. Hammick and L. W. Andrew.[19]   Mixtures of associated, of non-associated, and of associated with non-associated liquids were used, and it was found that the parachor is a linear function of the molecular fraction.   Anomalous results, however, were obtained with water as solvent.   The observed parachors of the lower members of the fatty-acid series have been found to be consistently low, whilst the reverse holds with the higher members of the series.[20]   S. Sugden's calculation of atomic and structural parachors has therefore been criticised [21] on the ground that the effect of chain branching has largely been ignored. His data have been recalculated using a slightly higher value for the mean parachor increment for the methylene group, and better agreement between observed parachors and those calculated with the revised constants is claimed, especially in compounds of high molecular weight.   With the new values, the parachor becomes more constitutive in character and is said to afford information as to the effects of intramolecular and interatomic stresses, for which allowance is made by the introduction of a strain constant.   The main conclusions drawn by Sugden and his co-workers, however, remain unaffected by the recalculations.

HAROLD HUNTER.

[18] *J.*, 1929, 1055.   [19] *Ibid.*, p. 754.
[20] K. W. Hunten and O. Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 153; *A.*, 252.
[21] S. A. Mumford and J. W. C. Phillips, *J.*, 1929, 2112.

INORGANIC CHEMISTRY.

It is becoming increasingly difficult to separate inorganic chemistry from physical chemistry, and whatever method of selection is used for this purpose, it may be open to criticism. An endeavour has been made to follow the line of division used in former years. The writers of all annual reports on chemistry are, however, faced with a far more serious difficulty, namely, the uneven quality of the great mass of literature which has to be considered.

All who have had much experience of chemical journals know that at the present time there are published many papers which are probably worthless, others simply restate facts which have long been known, while others, and this is true of many of those published in proprietary journals, should have been drastically curtailed before publication.

It seems time that these matters should be referred to. Much published work is valueless because it has been done in a careless and inefficient manner, and although the way in which it is described or the journal in which it is published will often suggest this, it is unfortunately not always obvious until one repeats the work oneself. In other cases, long lists of compounds are given without any analytical support, and results of experiments without any supporting data. There is nothing to show to what extent the " results " depend on the author's imagination and to what extent on experimental measurements. Many papers belonging to these two unsatisfactory classes have been referred to in the following Report, as it is scarcely justifiable to exclude them without stronger evidence than is usually available.

Atomic Weights and Separation of Isotopes.

Potassium.—The ratios KBr : Ag and KBr : AgBr gave 39·104 ± 0·0020 as the most probable value for the atomic weight of potassium.[1]

Copper.—From analyses of cupric chloride the atomic weight of copper was found to be 63·557 independently of its geographical origin.[2]

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[1] O. Hönigschmid and J. Goubeau, *Z. anorg. Chem.*, 1928, **177**, 102; *A.*, **369**.

[2] T. W. Richards and A. W. Phillips, *J. Amer. Chem. Soc.*, 1929, **51**, 400; *A.*, **370**.

Silver and Barium.—Full details of the determinations referred to in last year's annual report have been published.[3]

Cadmium.—Thirteen evaporations of cadmium in a vacuum failed to show any separation of isotopes.[4]

Boron.—It has been shown [5] that unless boric oxide glass is very carefully annealed it has too low a density. The variable densities obtained by Briscoe, Robinson, and Stephenson [6] cannot, therefore, be justifiably used as evidence of variation in the atomic weight of boron with its geographical source.

Cerium.—Analysis of cerium trichloride gave $140 \cdot 125 \pm 0 \cdot 007$ as the most probable value of the atomic weight of cerium.[7]

Uranium Lead and Protoactinium.—The mass spectrum of lead tetramethyl prepared from uranium lead shows only isotopes of mass numbers 206, 207, and 208, present in the proportions $86 \cdot 8$, $9 \cdot 3$, and $3 \cdot 9\%$. With a packing fraction [8] of $0 \cdot 8 \times 10^{-4}$, this corresponds to a mean atomic weight of $206 \cdot 19$. It is concluded that the line 207 corresponds with the end product of the disintegration of actinium. The mass number of protoactinium would then be fixed at 231, and extrapolation of the packing fraction curve then gives $231 \cdot 08$ for its exact atomic weight.[9]

Chlorine.—The ratio NOCl : Ag gave $35 \cdot 4565$ for the atomic weight of chlorine.[10] A fraction in which the chlorine had atomic weight $35 \cdot 418$ was obtained by diffusion of hydrogen chloride against air at atmospheric pressure through porous pipe-stems.[11] Fractional distillation of carbon tetrachloride showed no separation into fractions of different densities owing to the presence of different isotopes of chlorine.[12] Fractional distillation of large quantities of liquid chlorine, conversion of the fractions into ammonium chloride, and determination of the densities of the saturated solutions of the latter compound also failed to show any separation of chlorine isotopes.[13]

[3] O. Hönigschmid and R. Sachtleben, *Z. anorg. Chem.*, 1929, **178**, 1; *A.*, 370; *Ann. Reports*, 1928, **25**, 37.

[4] A. A. Sunier, *Abs. Theses Univ. Chicago*, Sci. Ser. 1925—1926, **4**, 173; *A.*, 115.

[5] A. Cousen and W. E. S. Turner, *J.*, 1928, 2654; *A.*, 22.

[6] *J.*, 1926, 70; *A.*, 1926, 219; *Ann. Reports*, 1926, **23**, 49.

[7] O. Hönigschmid and H. Holch, *Z. anorg. Chem.*, 1928, **177**, 91; *A.*, 370.

[8] *Ann. Reports*, 1928, **25**, 301.

[9] F. W. Aston, *Nature*, 1929, **123**, 313; *A.*, 370.

[10] A. F. Scott and C. R. Johnson, *J. Physical Chem.*, 1929, **33**, 1975.

[11] F. A. Jenkins, *Abs. Theses Univ. Chicago*, Sci. Ser., 1925—1926, **4**, 93; *A.*, 115.

[12] H. G. Grimm, *Z. physikal. Chem.*, 1929, [*B*], **2**, 181; *A.*, 484.

[13] H. G. Grimm and L. Braun, *ibid.*, p. 200; *A.*, 484.

Intensive Drying.

The minute details of manipulation and procedure essential for success in experiments on intensive drying have been described in two papers,[14] and experimental data on intensively dried liquids have been reviewed in another.[15] A book dealing with "The Effects of Moisture on Chemical and Physical Changes" has recently appeared.[16]

Superconductors.

Tantalum, thorium,[17] and gallium [18] have been added to the list of superconducting metals, the phenomenon commencing at 4·36°, 1·4°, and 1·07° Abs., respectively. It is pointed out that all the known superconducting elements occupy neighbouring places in the periodic table.

Since the superconductivity of tin at the temperature of liquid helium is not eliminated when the metal is enclosed in a tightly-fitting sheath of German silver, it is concluded that the phenomenon is a volume rather than a surface effect, and from other experiments it is concluded that the current is carried by electrons distributed at random and that the disappearance of resistance is due to the failure of the electrons to give up their energy to the atoms owing to elastic reflexion.[17]

Compounds of a superconducting metal with a non-superconductor may be superconductors. This is true of the compounds Bi_5Tl_3, Sb_2Tl_7, SbSn, Sb_2Sn_3, and $AuPb_2$, in which only thallium, tin, and lead are superconductors in the pure state.[19] Antimony and zinc also yield a superconducting alloy.[20] In exceptional cases, as with certain alloys of gold and bismuth, it appears to be possible to get superconducting mixtures from two metals neither of which is a superconductor.[21] Copper sulphide (CuS) has the distinction of being the first ordinary simple compound that has been found to be a superconductor.[22]

[14] See this vol., p. 27.

[15] J. W. Smith, *Phil. Mag.*, 1929, [vii], **8**, 380; *A.*, 1226.

[16] By J. W. Smith (Longmans, Green & Co., Ltd., 1929).

[17] W. Meissner, *Physikal. Z.*, 1928, **29**, 897; *A.*, 250; *Naturwiss.*, 1929, **17**, 390; *A.*, 871.

[18] W. J. de Haas and J. Voogd, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 214, 733; *A.*, 496, 1135.

[19] E. van Aubel, W. J. de Haas, and J. Voogd, *ibid.*, pp. 218, 731; *A.*, 496, 1136; W. J. de Haas, *Nature*, 1929, **123**, 130; *A.*, 385.

[20] W. J. de Haas, *Naturwiss.*, 1929, **17**, 85; *A.*, 250.

[21] W. J. de Haas, E. van Aubel, and J. Voogd, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 226, 724; *A.*, 652, 1135; W. J. de Haas, *Naturwiss.* 1929, **17**, 85; *A.*, 250.

[22] W. Meissner, *Z. Physik*, 1929, **58**, 570; *A.*, 1930, 22.

The superconductivity of thallium in magnetic fields [23] has been studied, as also the resistance of various alloys at the temperatures of liquid hydrogen and liquid helium.[24]

X-Rays and Chemical Problems.

The crystal structure of many compounds and mixtures, both simple and complex, has been examined of recent years by means of X-rays, but it may be doubted whether the conclusions which are often drawn as to chemical structure are always justified by the observations. Very few of these papers can even be referred to here, although in some cases, undoubtedly, X-rays can give useful help to the chemist.

Some support has been obtained for the existence of sub-ions from observations on silver subfluoride, which appears to have a structure in which the atomic diameter of silver with respect to silver and with respect to fluorine is equal to the atomic diameter of silver in the metallic state and in normal combination, respectively.[25] Copper amalgams appear to be merely mechanical mixtures of the two metals so long as they are soft, but when an amalgam sets there is a change in structure and a definite compound is formed.[26] Cobaltous and magnesium orthostannates have been prepared by precipitating suitable mixtures of cobalt or magnesium and stannic chlorides with sodium hydroxide and calcining the precipitates at 900°. X-Ray examination shows that the products so obtained, viz., $M_2^{II}M^{IV}O_4$, are true spinels and correspond in every structural particular with the more usual type of spinel $M^{II}M_2^{III}O_4$.[27]

The nature of the precipitates obtained from mixed salt solutions is of some interest. Mixed hydroxides have been examined by X-rays and found to consist of solid solutions if the kations of the two constituent hydroxides do not differ widely in radius; otherwise the precipitate is a simple mixture. Thus nickel hydroxide forms solid solutions with the hydroxides of magnesium, zinc, and cobalt, but not with those of cadmium or calcium.[28] X-Ray examination has shown the complete miscibility of the oxides in the systems CoO–MgO, NiO–MgO, and CoO–NiO.[29]

[23] W. Tuyn, *Proc. K. Akad. Wetensch. Amsterdam*, 1928, **31**, 687; *A.*, 250.

[24] W. J. de Haas, E. van Aubel, and J. Voogd, *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 715; *A.*, 1135.

[25] H. Terrey and H. Diamond, *J.*, 1928, 2820; *A.*, 16.

[26] H. Terrey and C. M. Wright, *Phil. Mag.*, 1928, [vii], **6**, 1055; *A.*, 16.

[27] G. Natta and L. Passerini, *Atti R. Accad. Lincei*, 1929, [vi], **9**, 557; *A.*, 780.

[28] *Idem, Gazzetta*, 1928, **58**, 579; *A.*, 1928, 1316.

[29] S. Holgersson and A. Karlsson, *Z. anorg. Chem.*, 1929, **182**, 225; *A.*, 1130.

Zinc oxide and silica begin to react at 775° and the orthosilicate, Zn_2SiO_4, is always obtained even although the constituent oxides are used in the proportion required for the metasilicate, $ZnSiO_3$.[30] " Titanium cyanonitride," found in blast furnaces, is of doubtful nature : X-ray data are said to support the view that it consists of mixed crystals of titanium carbide and nitride,[31] although chemical work shows that it is probably titanium nitride with intermingled graphite.[32]

Considerable X-ray activity continues in connexion with metallography. Two borides of iron, Fe_2B and FeB, appear to occur in iron–boron alloys containing from 0 to 19% of boron.[33] Chromium containing nitrogen shows the existence of two nitrogenous phases. In the one the chromium atoms are densely packed in a hexagonal lattice, the nitrogen atoms probably being distributed at random in the hollow spaces of the lattice ; this phase varies in composition up to one approaching that required by the formula Cr_2N. The second phase has the sodium chloride structure and corresponds with the compound CrN. In a ferrochrome containing 2·4% of nitrogen, the latter was mainly present as the hexagonal Cr–N phase.[34] X-Ray observations on copper–antimony alloys[35] agree with the equilibrium diagram for the system obtained by Carpenter,[36] but those on the silver–antimony system show that Petrenko's equilibrium diagram is incorrect.[37]

Alloys of zinc with iron are closely similar in their crystalline forms to its alloys with silver, copper, and gold : two compounds, Fe_3Zn_{10} and $FeZn_7$, are apparently formed.[38]

Corrosion and Passivity of Metals.

Several important papers on the corrosion of metals have been published during the past year. In the case of atmospheric corrosion, it is concluded that there is a critical humidity for each metal, determined by the nature of its corrosion products, above which condensation will occur on the surface, such condensation probably being essential for corrosion. The amount of corrosion of different

[30] A. Pabst, Z. physikal. Chem., 1929, **142**, 227 ; A., 996.

[31] V. M. Goldschmidt, Nachr. Ges. Wiss. Göttingen, 1927, 390 ; Chem. Zentr., 1928, i, 1541, 2692 ; A., 18, 524.

[32] E. A. Rudge and F. Arnall, J. Soc. Chem. Ind., 1928, **47**, 376T.

[33] T. Bjurström and H. Arnfelt, Z. physikal. Chem., 1929, [B], **4**, 469 ; A., 1138.

[34] R. Blix, ibid., **3**, 229 ; A., 747.

[35] A. Westgren, G. Hägg, and S. Eriksson, ibid., **4**, 453 ; A., 1139.

[36] Z. Metallk., 1913, **4**, 300.

[37] Z. anorg. Chem., 1906, **50**, 139.

[38] A. Ôsawa and Y. Ogawa, Sci. Rep. Tôhoku Imp. Univ., 1929, **18**, 165 ; A., 1130.

non-ferrous metals and alloys under various atmospheric conditions was determined in several ways.[39] The corrosion of spirals of pure iron wire in various atmospheres of dry or moist air, oxygen, carbon dioxide, and mixtures of the last two has been investigated. A film of liquid water adhering to the metal seems essential; in this the iron is supposed to dissolve as ferrous hydroxide till the p_H is 9·4. The oxygen and carbon dioxide, by oxidation and formation of ferrous carbonate, act as depolarisers and so accelerate the corrosion.[40] Much higher hydrogen pressures are reached in the reaction between iron and water than electrochemical data suggest, and it is inferred. that this is due to the decomposition of water by ferrous hydroxide.[41] When air-free water and ferric hydroxide act upon iron filings, hydrogen is evolved, and the ferric hydroxide is blackened owing to conversion into triferric tetroxide.[42] Hydrogen peroxide is formed when iron amalgam rusts in water, still larger amounts being formed in presence of alkali; with iron powder (ferrum reductum) the hydrogen peroxide can only be detected when alkali is used. The part played by the peroxide in the rusting of iron is discussed.[43] The importance of differential aëration and the breakdown of protective films as factors in the corrosion of metals has been emphasised and demonstrated.[44] The importance of oxygen supply in cases of corrosion of one metal in contact with a nobler metal has also been shown. Measurement of the electrical currents between the two metals gives a quick and simple indication of the corrosive properties of the solutions.[45] Potential differences between adjacent portions of metal play an important part in the corrosion and dissolution of metals.[46]

Potential measurements show that, with care, iron can be made to corrode in a stable and reproducible manner. Time–potential curves show that the film present on iron after exposure to air increases its resistance to destruction by the electrolyte.[47] The presence of oxide films, often invisible, on many metals has now been demonstrated, in many cases by the separation and isolation of the films; that the presence of such a film is the normal cause

[39] J. C. Hudson, Atmospheric Corrosion of Metals, Third (Experimental) Report to the Atmospheric Corrosion Research Committee (British Non-ferrous Metals Research Association), 1929; *B.*, 684.

[40] J. F. G. Hicks, *J. Physical Chem.*, 1929, **33**, 780; *B.*, 521.

[41] G. Schikorr, *Z. Elektrochem*, 1929, **35**, 62; *A.*, 266.

[42] A. Schikorr, *ibid.*, p. 65; *A.*, 283.

[43] H. Wieland and W. Franke, *Annalen*, 1929, **469**, 257; *B.*, 476.

[44] U. R. Evans, *J.*, 1929, 92, 111; *A.*, 270, 271.

[45] F. Tödt, *Z. Elektrochem.*, 1928, **34**, 586, 591, 853; *A.*, 145, 145, 270.

[46] W. Palmaer and others, *Handl. Ing. Vetenskaps-Akad. Stockholm*, 1929, No. 93; *B.*, 921.

[47] A. L. McAulay and S. H. Bastow, *J.*, 1929, 85; *A.*, 270.

of passivity is becoming generally accepted.[48]   The electrolytic formation of protective films and its bearing on the question of passivity has been studied.[49]

The theory that the phenomena of passivity are due to valency changes still survives.[50]   It has also been suggested that crystal structure plays a part.[51]

Group O.

The m. p.–pressure curve of helium has been followed up to a temperature of 42° Abs. where the corresponding pressure is 5600 kg./sq. cm.[52]

When a discharge is passed through helium at several mm. pressure between platinum electrodes, the deposit formed on the tube contains large quantities of adsorbed or combined helium. The observed diminution of pressure in the tube corresponded to the adsorption of 14—34 c.c. per g. of platinum deposited.[53]   F. Paneth and K. Peters [54] describe unsuccessful attempts to prepare helium compounds, and show how the diffusion of helium through glass can be utilised to prepare neon-free helium.   Hydrogen and helium may be easily separated by causing the former to diffuse through palladium.

Group I.

One of the most striking results of the past year is the separation of the two forms of molecular hydrogen predicted by the wave-mechanics.   These are characterised by symmetrical and anti-symmetrical functions, and the terms para- and ortho- have been used to distinguish these states, although Sir E. Rutherford would prefer to designate them α and β.[55]

[48] J. Hinnüber, Z. Elektrochem., 1929, **35**, 95; A., 270; U. R. Evans and J. Stockdale, J., 1929, 2651; A. M. Haselrink, Z. Elektrochem., 1928, **34**, 819; A., 146; L. C. Bannister, J., 1928, 3163; A., 158; U. R. Evans, J., 1927, 1020; A., 1927, 619; Ann. Reports, 1927, **24**, 58; U. R. Evans, Nature, 1929, **123**, 16; A., 134; F. H. Constable, Nature, 1929, **123**, 569; A., 520; L. Tronstad, ibid., **124**, 373; A., 1150; Z. physikal. Chem., 1929, **142**, 241; A., 1012.

[49] W. J. Müller and K. Konopicky, Monatsh., 1928, **50**, 385; 1929, **52**, 289; A., 146, 1241; W. J. Müller and O. Löwy, ibid., **51**, 73; A., 402; W. J. Müller, Z. Elektrochem., 1929, **35**, 93, 656; A., 270, 1393.

[50] R. Müller, ibid., p., 459; A., 1016.

[51] J. N. Stranski and Z. C. Mutaftschiew, ibid., p. 393; A., 1016.

[52] F. Simon, Naturwiss., 1929, **17**, 256; A., 636; F. Simon, M. Ruhemann, and W. A. M. Edwards, Z. physikal. Chem., 1929, [B], **2**, 340; [B], **6**, 62; A., 497; 1930, 24.

[53] H. Damianovich, Anal. Fis. Quim., 1928, **26**, 365; A., 156; Compt. rend., 1929, **188**, 790; A., 523; H. Damianovich and J. J. Trillat, ibid., p. 991; A., 523.

[54] Z. physikal. Chem., 1928, [B], **1**, 253; A., 25.

[55] Pres. Address to Royal Society, Nov. 30th, 1929; see Nature, 1929, **124**, 878.

The specific heat of hydrogen changes with temperature in a way which could not be explained by the older theories. This is due to a gradual change in the proportion of the two forms present.[56]

K. F. Bonhoeffer and P. Harteck [57] have studied the interconversion of para- and ortho-hydrogen very fully. The changes are most readily followed by measuring the change in resistance of a heated wire in presence of the gas, which varies with the specific heat of the latter. Hydrogen in equilibrium at ordinary temperatures consists of about 25% para- and 75% ortho-. At liquid-air temperatures, the equilibrium is very largely in favour of the para-form, and probably would be almost entirely so at liquid-helium temperatures. Equilibrium is established very slowly in the pure gas phase, but very rapidly when the gas is adsorbed on platinised asbestos or, still better, on charcoal, especially under pressure. In this way para-hydrogen has been obtained practically pure, and will remain so for a long time at the ordinary temperature in absence of catalysts like charcoal. The ortho-form has not been obtained pure. The specific heat of para-hydrogen at low temperatures is greater than that of ortho-hydrogen. There is a large evolution of heat during the passage of ortho- to para-hydrogen. The strong lines in the para-hydrogen emission spectrum are the weak ones in the emission spectrum of ordinary hydrogen. Attempts to separate para- and ortho-forms of water by fractionation at low temperatures were unsuccessful, and this is attributed to the high velocity of transformation of one form into the other.[58]

A. Smits [59] regards the discovery of para- and ortho-hydrogen as an experimental realisation of certain aspects of his theory of allotropy.

The formation of monatomic hydrogen from hydrogen molecules by collision with electrons of 7—16 volts energy has been studied by K. E. Dorsch and H. Kallmann.[60] The reaction $2H = H_2$ has been followed calorimetrically.[61] The action of atomic hydrogen on hydrocarbons seems to be very complex.[62]

[56] A. Eucken, *Naturwiss.*, 1929, **17**, 182; *A.*, 497; A. Eucken and K. Hiller, *Z. physikal. Chem.*, 1929, [B], **4**, 142; *A.*, 990; K. Clusius and K. Hiller, *ibid.*, p. 158; *A.*, 990.

[57] *Naturwiss.*, 1929, **17**, 182, 321; *A.*, 479, 732; *Z. physikal. Chem.*, 1929, [B], **4**, 113; [B], **5**, 292; *A.*, 982, 1218; *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1929, 103; *A.*, 732; *Z. Elektrochem.*, 1929, **35**, 621; *A.*, 1372.

[58] K. F. Bonhoeffer and P. Harteck, *Z. physikal. Chem.*, 1929, [B], **5**, 293; *A.*, 1218.

[59] *Physikal. Z.*, 1929, **30**, 425; *A.*, 982.

[60] *Z. Physik*, 1929, **53**, 80; *A.*, 483.

[61] H. M. Smallwood, *J. Amer. Chem. Soc.*, 1929, **51**, 1985; *A.*, 1016.

[62] K. F. Bonhoeffer and P. Harteck, *Z. physikal. Chem.*, 1928, **139**, 64; *A.*, 409; H. S. Taylor and D. G. Hill, *ibid.*, 1929, [B], **2**, 449; *A.*, 655; A. Klemenc and F. Patat, *ibid.*, **3**, 289; *A.*, 892.

Under high pressure, hydrogen will displace metallic copper from solutions of its salts, but as, in all circumstances, there is an equilibrium between cupric and cuprous salt and metallic copper, the displacement is never complete.[63] The reducing action of hydrogen under high pressure on pentachlororuthenates has also been studied.[64]

When lithium carbonate and sodium carbonate are decomposed in boiling aqueous solution the amount transformed into hydroxide is proportional to the square root of the time.[65] The solubility of sodium in sodium chloride is said to be 4·2% at 800° and 15—20% at 850°, whilst at higher temperatures the metal phase disappears.[66]

By treating sodium dissolved in liquid ammonia with lead iodide, or by extracting an alloy of lead and sodium with liquid ammonia, compounds of the type Na_4Pb_7 and Na_4Pb_9 are obtained. All elements of the long periods of the periodic system which are 1—4 positions removed from a rare gas and form liquid hydrides will give such compounds with sodium; these have the characteristics of salts, probably have a polysulphide-like structure, and crystallise from ammonia in the form $[Na(NH_3)_y]_n{}^+ [X^{n-}(X)_x]$. X-Ray observations show that in the ammonia-free form there is a complete change of structure with formation of an intermetallic phase containing no chemical compound.[67] $NaZn_4$ is formed by the action of sodium on zinc cyanide dissolved in liquid ammonia.[68]

The precipitate obtained by the action of potassium salts on solutions of sodium cobaltinitrite has a constant composition corresponding with the formula $[Co(NO_2)_6]K_2Na,nH_2O$ (where n is generally 1) so long as the ratio Na/K is above about 25. As the ratio falls below this value, the amount of potassium in the precipitate increases and gradually approaches that required for the compound $[Co(NO_2)_6]K_3,nH_2O$. For a given Na/K ratio the precipitate is richer in potassium the higher the temperature of precipitation.[69]

Rubidium chloride, bromide, and iodide are converted at high pressures into a second modification.[70]

[63] V. Ipatiev and V. Ipatiev, jun., *Ber.*, 1929, **62**, [*B*], 386; *A.*, 410.

[64] V. N. Ipatiev and O. E. Zvjaginstsev, *ibid.*, p. 708; *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 823; *A.*, 527, 1029.

[65] B. L. Vanzetti, *Gazzetta*, 1929, **59**, 219; *A.*, 661; B. L. Vanzetti and A. Oliverio, *ibid.*, pp. 288, 300; *A.*, 887.

[66] R. Lorenz and R. Winzer, *Z. anorg. Chem.*, 1929, **183**, 121; *A.*, 1229.

[67] E. Zintl, *Naturwiss.*, 1929, **17**, 782; *A.*, 1249.

[68] W. M. Burgess and A. Rose, *J. Amer. Chem. Soc.*, 1929, **51**, 2127; *A.*, 1154.

[69] L. Bonneau, *Bull. Soc. chim.*, 1929, [iv], **45**, 798; *A.*, 1930, 49.

[70] P. W. Bridgman, *Z. Krist.*, 1928, **67**, 363; *Chem. Zentr.*, 1928, ii, 317; *A.*, 140.

Element 87 (ekacæsium) has been searched for by a positive-ray method in products obtained from pollucite and lepidolite. It was not present to an extent greater than 3.5×10^{-7} and 7.3×10^{-6} in the cæsium separated from the two minerals, respectively.[71]

A number of ammines of cupric nitrite have been obtained.[72] Pure cupric sulphide has been prepared, as a dark blue substance soluble in potassium cyanide, by the union of finely divided copper and sulphur prepared at low temperatures; the mixture was heated by steam in a bomb tube containing carbon disulphide.[73] The sulphide precipitate obtained by the action of cupric salts on sodium thiosulphate is a mixture of cuprous and cupric sulphides and free sulphur.[74] Cuprous sulphide reacts with ferric sulphate in two stages; the first, $Cu_2S + Fe_2(SO_4)_3 = CuS + CuSO_4 + 2FeSO_4$, predominates at ordinary temperatures, but at higher temperatures it is followed by a second reaction: $CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S$.[75] A method of obtaining cuprous sulphate from copper and sulphuric acid has been described.[76] Cuprous iodide has a vapour density at 900—1100° corresponding with the formula CuI, whereas the bromide has the double formula.[77] A number of complex dicarboxylic acid salts of copper have been prepared which are said to have the structure $Na_2[CuX_2(H_2O)_2]$ and to contain copper with a co-ordination number of six.[78] The solutions obtained by adding sodium hydroxide to solutions containing copper or iron salts in presence of various hydroxylic organic substances were examined by ultra-filtration and other methods; it is concluded that the dissolved metal is present partly as a colloid and partly as a crystalloid complex in proportions which depend on the conditions.[79] Fehling's solution is considered to be essentially colloidal in nature.[80]

The ratio of the hydroxyl- and chloride-ion concentrations when silver oxide has reached equilibrium with potassium chloride solutions at 25° is independent of the method of preparation of the oxide [81] and is substantially the same as that found by Noyes and Kohr.[82] A crystalline compound $Na_6[AgI(CNS)_6]$ has been obtained

[71] K. T. Bainbridge, *Physical Rev.*, 1929, [ii], **34**, 752; *A.*, 1210.

[72] H. J. S. King, *J.*, 1929, 2593; *A.*, 1930, 47.

[73] K. Fischbeck and O. Dorner, *Z. anorg. Chem.*, 1929, **182**, 228; *A.*, 1250.

[74] J. Hanuš and V. Hovorka, *J. Czech. Chem. Comm.*, 1929, **1**, 65; *A.*, 410.

[75] L. Whitby, *J.*, 1929, 60; *A.*, 283.

[76] J. G. F. Druce and G. Fowles, *Chem. News*, 1928, **137**, 385; *A.*, 156.

[77] K. Jellinek and A. Rudat, *Z. physikal. Chem.*, 1929, **143**, 55; *A.*, 1226.

[78] H. L. Riley, *J.*, 1929, 1307; *A.*, 896.

[79] W. Bachmann, *Kolloid-Z.*, 1929, **47**, 49; *A.*, 260.

[80] H. Dumanski and A. A. Chalisev, *ibid.*, p. 121; *A.*, 259.

[81] R. F. Newton, *J. Amer. Chem. Soc.*, 1928, **50**, 3258; *A.*, 141.

[82] *A.*, 1903, ii, 201.

by refluxing an acetone solution of sodium thiocyanate with silver iodide; the compounds $K_6[AgI(CNS)_6]$ and $(NH_4)_8[AgI(CNS)_8]$ were also prepared.[83]   Silver dissolves to a considerable extent in dilute ammonia on account of the relatively stable $Ag(NH_3)_2OH$ complex facilitating atmospheric oxidation.   The dissolution gets slower and slower and finally stops after some months, long before the ammonia is saturated with respect to silver oxide; it is concluded that this is due to the slow formation of silver fulminate or similar products, $e.g.$, Ag_3N or Ag_2NH, which are gradually deposited on the surface of the metal.[84]

The dissociation pressures of aurous chloride and bromide and auric chloride have been determined at various temperatures.   No evidence could be obtained for the existence of gold dichloride or of a double compound between it and potassium chloride.[85]   The system gold–chlorine has been investigated up to 1250° at 1 atm. pressure of chlorine; above 475° the vapour phase contains Au_2Cl_2 molecules.[86]   The auric chloride molecule is Au_2Cl_6 at 250°.[87]

Group II.

There has been much activity in connexion with beryllium.   The commercial production of the metal on the scale of one ton per annum is about to occur.[88]   The metal is produced by electrolysis of a mixed electrolyte prepared from $2BeO,BeF_2$ and barium fluoride and containing about 45% of the latter.   Electrolysis is carried out at 1400° with a current density of 100—400 amps./cm.^{2} of cathode area, a graphite crucible serving as anode and a water-cooled iron tube as cathode.[89]   The metal can be plated electrolytically on to other metals from fused baths.[90]   The $2BeO,BeF_2$ required for the above process is obtained from beryl by a method [91] which gives nearly a 90% yield of pure product : the finely powdered mineral is heated to 650° for several hours with sodium silicofluoride, the product leached, the resulting Na_2BeF_4 precipitated with lime in slight excess, the beryllium hydroxide obtained is separated from calcium fluoride by solution in hydrofluoric acid, the solution evaporated to dryness, and the residue heated to 150°.   An account

[83]   A. C. Vournasos, *Z. anorg. Chem.*, 1929, **182**, 37; *A.*, 1153.

[84]   K. A. Hofmann and U. Hofmann, *Ber.*, 1928, **61**, [*B*], 2566; *A.*, 156.

[85]   W. Fischer and W. Biltz, *Z. anorg. Chem.*, 1928, **176**, 81; *A.*, 31.

[86]   W. Biltz, W. Fischer, and R. Juza, *ibid.*, p. 121; *A.*, 31.

[87]   W. Fischer, *ibid.*, 1929, **184**, 333.

[88]   A. Stock, *Z. angew. Chem.*, 1929, **42**, 637.

[89]   K. Illig, M. Hosenfeld, and H. Fischer, *Wiss. Veröff. Siemens-Konz.*, 1929, **8**, (1), 42; *B.*, 722; H. Fischer, *ibid.*, p. 59; *B.*, 723.

[90]   H. Fischer, *ibid.*, p. 83; *B.*, 723.

[91]   K. Illig, M. Hosenfeld, and H. Fischer, *ibid.*, p. 30; *B.*, 722.

has been published of older methods of obtaining beryllium,[92] and also a review of the literature dealing with the physical properties of the element and much of its chemical behaviour.[93] There are two crystalline forms of beryllium hydroxide. Monosodium beryllate, $BeO,NaOH,H_2O$, is the stable solid phase at 30° in contact with solutions of sodium hydroxide containing above 35% of the latter.[94] The preparation of beryllium chloride from beryl is described by W. Winters and L. F. Yntema,[95] and that of beryllium oxide by H. A. Sloman,[96] while J. M. Schmidt [97] has made a detailed study of the chloride and of its combination with other chlorides. Hydrated beryllium chloride and bromide have been prepared by V. Čupr and H. Šalanský.[98]

Very pure magnesium has been made commercially by subliming the ordinary metal at 600° under a pressure of 0·5—1·5 mm.[99] The solubilities of magnesium hydroxide [1] and carbonate [2] have been examined.

The m. p.'s of calcium, strontium, and barium are 810°, 752°, and 658° respectively.[3]

Solubilities have been recorded for calcium hydroxide [4] and calcium sulphate [5] in water, for calcium carbonate in solutions of carbon dioxide, gypsum, and sodium chloride,[6] and for calcium phosphates in sulphurous acid.[7] The hydrolysis of calcium phosphate and the adsorption of lime by basic calcium phosphate have been examined,[8] and the existence of two suspiciously complex calcium sulphoaluminates has been announced.[9] The action of bromine on strontium oxide and its hydrates has been examined in

[92] K. Illig and M. Hosenfeld, *Wiss. Veröff. Siemens-Konz.*, 1929, **8**, (1), 26; *A.*, 1024.

[93] K. Illig, *ibid.*, p. 74; *A.*, 1024.

[94] R. Fricke and H. Humme, *Z. anorg. Chem.*, 1929, **178**, 400; *A.*, 399.

[95] *Trans. Amer. Electrochem. Soc.*, 1929, **55**, 205; *B.*, 641.

[96] *J. Soc. Chem. Ind.*, 1929, **48**, 309T; *B.*, 1043.

[97] *Ann. Chim.*, 1929, [x], **11**, 351; *A.*, 1024.

[98] *Z. anorg. Chem.*, 1928, **176**, 241; *A.*, 38.

[99] H. E. Bakken, *Chem. Met. Eng.*, 1929, **36**, 345; *B.*, 685.

[1] A. Travers and Nouvel, *Compt. rend.*, 1929, **188**, 499; *A.*, 388.

[2] W. D. Kline, *J. Amer. Chem. Soc.*, 1929, **51**, 2093; *A.*, 997.

[3] H. Hartmann and G. May, *Z. anorg. Chem.*, 1929, **185**, 167.

[4] L. B. Miller and J. C. Witt, *J. Physical Chem.*, 1929, **33**, 285; *A.*, 388.

[5] E. P. Partridge and A. H. White, *J. Amer. Chem. Soc.*, 1929, **51**, 360; *A.*, 388.

[6] G. L. Frear and J. Johnston, *ibid.*, p. 2082; *A.*, 997.

[7] W. M. Mebane, J. T. Dobbins, and F. K. Cameron, *J. Physical Chem.*, 1929, **33**, 961; *A.*, 997.

[8] J. R. Lorah, H. V. Tartar, and (Miss) L. Wood, *J. Amer. Chem. Soc.*, 1929, **51**, 1097; *A.*, 777.

[9] W. Lerch, F. W. Ashton, and R. H. Bogue, *U.S. Bur. Stand. Res. Paper*, 1929, No. 54; *Bur. Stand. J. Res.*, 1929, **2**, 715; *A.*, 662.

some detail.[10]   Strontium thiosulphate and strontium and barium tetrathionates [11] have been prepared and described.

The use of barium perchlorate as a drying agent and absorbent of ammonia is recommended by G. F. Smith,[12] and the fractionation of barium–radium solutions has been investigated by Z. T. Walter and H. Schlundt.[13]

Careful studies have been made of the distribution of radium nitrate between crystalline barium nitrate and its saturated solutions at 0° and 25°, also between mixed crystals of barium and lead nitrates and the corresponding saturated aqueous solutions. The Berthelot–Nernst distribution law was found to hold.[14]

The dehydration of $3CdSO_4,8H_2O$ has been studied by L. Coniglio, who found that $3CdSO_4,5H_2O$, $3CdSO_4,2H_2O$, and $3CdSO_4,H_2O$ are formed as stages between it and the anhydrous salt.[15]

Cadmium peroxides have been prepared by several methods. There are considered to be at least two definite compounds, $Cd_4O_7,2H_2O$ and $3CdO,2H_2O_2$.[16]

A number of complex salts of o-phenylenediamine and o-tolylenediamine with zinc and cadmium halides have been prepared, some of which are octammines. All are brightly coloured compounds and several exist in two forms which are probably stereoisomerides.[17]

Mercury-vapour pressure and calorimetric measurements have been made on a number of amalgams, and several definite compounds of mercury with sodium, gold, thallium, and cerium are indicated.[18]

There are two definite compounds of ammonia with mercuric iodide, $HgI_2,2NH_3$ and $3HgI_2,4NH_3$; their reactions with aqueous ammonia leading to Hg_2NI and $Hg_9N_4I_6$ have been fully investigated.[19]   Contrary to statements of earlier workers, mercuric chloride and bromide combine with dry gaseous ammonia to yield $HgCl_2,2NH_3$ and $HgBr_2,2NH_3$.[20]

The decomposition of mercurous chloride in concentrated alkali

[10] H. B. Dunnicliff, H. D. Suri, and K. L. Malhotra, *J.*, 1928, 3106; *A.*, 157.

[11] R. Portillo, *Anal. Fis. Quím.*, 1929, **27**, 236, 243, 351; *A.*, 778, 896.

[12] *Chemist-Analyst*, 1929, **18**, 18; *A.*, 1026.

[13] *J. Amer. Chem. Soc.*, 1928, **50**, 3266; *A.*, 132.

[14] V. Chlopin, A. Polessitsky, and P. Tolmatscheff, *Z. physikal. Chem.*, 1929, **145**, 57, 67.

[15] *Rend. Accad. Sci. Fis. Mat. Napoli*, 1928, [iii], **34**, 119; *A.*, 279.

[16] T. R. Perkins, *J.*, 1929, 1687; *A.*, 1154.

[17] W. Wahl, *Förh. III nord. Kemistmötet*, 1928, 172; *A.*, 157.

[18] W. Biltz and F. Meyer, *Z. anorg. Chem.*, 1928, **176**, 23; *A.*, 31.

[19] M. François, *Ann. Chim.*, 1929, **11**, 22; *A.*, 524.

[20] *Idem, Compt. rend.*, 1929, **188**, 1500; *Bull. Soc. chim.*, 1929, [iv], **45**, 616; *A.*, 896, 1250.

chloride solutions has been studied and considered with reference to the irregularities of the calomel cell.[21] Various reactions of infusible white precipitate, $HgCl,NH_2$, and of fusible white precipitate, $HgCl_2,2NH_3$, have been compared.[22]

J. M. Walter and S. Barratt [23] have shown that the majority of the band spectra associated with zinc, cadmium, and mercury are in reality due to traces of impurities such as oxide and chloride. There is no doubt, however, that mercury vapour contains some diatomic molecules.

Group III.

The difficult problem of the structure of the boron hydrides continues to attract investigators. F. Ephraim [24] considers that they can be satisfactorily explained on the octet theory of distribution of the outer electrons, but in his suggested structures some electrons are shared between three atoms, which will doubtless be considered unsatisfactory. W. Hellriegel [25] suggests that the two inner electrons of the boron atom are displaced so as to produce an octet with the other six in the group BH_3. These inner electrons are involved in the union of the two BH_3 groups to form B_2H_6. $B(CH_3)_3$ and $B(C_2H_5)_3$ exist as such and do not polymerise; their great reactivity towards oxygen is, however, attributed to the same cause as that giving rise to polymerisation of BH_3. Structures for all the boron hydrides are put forward. A. Stock and E. Pohland [26] have published a paper on the more complex boron hydrides; it is mainly concerned with the physical and chemical properties of $B_{10}H_{14}$.

Vapour pressure measurements indicate the existence of eight boric acids nB_2O_3,H_2O, where $n = 1$—8.[27] BF_3,NH_3 and its three ethyl derivatives have been prepared as white solids by treating an ethereal solution of BF_3 with ammonia or the appropriate amine.[28]

$K_2BeF_4,Al_2(SO_4)_3,24H_2O$ and $K_2ZnCl_4,Al_2(SO_4)_3,24H_2O$ are two representatives of an interesting new type of alum.[29] The equilibrium $4AlN + 3C = Al_4C_3 + 2N_2$ has been studied between 1774°

[21] T. W. Richards and M. Françon, *J. Physical Chem.*, 1929, **33**, 936; *A.*, 887.

[22] P. Rây and P. Banerji, *J. Indian Chem. Soc.*, 1928, **5**, 715; *A.*, 279.

[23] *Proc. Roy. Soc.*, 1929, [*A*], **122**, 201; *A.*, 237.

[24] *Helv. Chim. Acta*, 1928, **11**, 1094; *A.*, 123.

[25] *Z. anorg. Chem.*, 1929, **185**, 65.

[26] *Ber.*, 1929, **62**, [*B*], 90; *A.*, 279.

[27] L. F. Gilbert and (Miss) M. Levi, *J.*, 1929, 527; *A.*, 491.

[28] C. A. Kraus and E. H. Brown, *J. Amer. Chem. Soc.*, 1929, **51**, 2690; *A.*, 1250.

[29] W. R. C. Curjel, *Nature*, 1929, **123**, 206; *A.*, 246.

and 1909° Abs.[30]   By the action of aluminium triethyl on water, aluminium hydroxide of composition corresponding to the formula $Al(OH)_3$ has been obtained either as a gelatinous precipitate or as a fine granular one.[31]   J. Hoffmann [32] has published a long paper on ultramarine, in which are some interesting experiments, novel views, and a useful summary of theories and literature on this puzzling substance, or, rather, group of substances.   A product resembling kaolin has been prepared by precipitating alumina and silica together in the correct proportion and treating the dried precipitate with steam for 12 days under a pressure of 200— 260 atm.[33]   The dissociation pressure of kaolin is a function of the water content over the whole range.[34]

The formation of gallium oxalate, basic gallium acetate, and basic gallium ammonium sulphate is described by A. Tchakirian.[35]

W. Klemm has considered the classification of the rare-earth elements in terms of their electronic configuration, and shows that there is within the group a certain periodicity of chemical properties as well as of physical ones such as the ionic susceptibility and colour of oxides or ions.[36]   These considerations showed that ytterbium dichloride should exist, and it has in fact been readily obtained by reduction of the trichloride with hydrogen at 600—900°.   The dichloride is colourless, relatively very stable towards water and ammonia, and similar in many respects to strontium chloride.[37]

A full and careful account of the scandium oxalates and double oxalates has been given,[38] while a detailed study has been made of samarium chloride–ammonia complexes.[39]   The oxides of the ceria-earth metals have been studied with special reference to the influence of temperature and oxygen pressure on the composition.   Only cerium and praseodymium appear to form higher oxides.[40]   The anhydrous iodides of the elements of the ceria earths have been

[30] C. H. Prescott, jun., and W. B. Hincke, *J. Amer. Chem. Soc.*, 1928, **50**, 3228; *A.*, 142.

[31] P. A. Thiessen and K. L. Thater, *Z. anorg. Chem.*, 1929, **181**, 417; *A.*, 1026.

[32] *Ibid.*, **183**, 37.

[33] C. J. van Nieuwenburg and H. A. J. Pieters, *Rec. trav. chim.*, 1929, **48**, 27: *A.*, 280.

[34] *Idem, ibid.*, p. 406; *A.*, 636.   [35] *Compt. rend.*, 1929, **189**, 251; *A.*, 1026.

[36] *Z. anorg. Chem.*, 1929, **184**, 345.

[37] W. Klemm and W. Schüth, *ibid.*, p. 352.

[38] J. Štěrba-Böhm and S. Škramovský, *Časopis Českoslov. Lék.*, 1928, **8**, 211; *Chem. Zentr.*, 1929, i, 2399; *J. Czech. Chem. Comm.*, 1929, **1**, 1; *A.*, 1251, 541.

[39] W. Klemm and J. Rockstroh, *Z. anorg. Chem.*, 1928, **176**, 181; *A.*, 38.

[40] H. A. Pagel and P. H. M.-P. Brinton, *J. Amer. Chem. Soc.*, 1929, **51**, 42; *A.*, 280.

prepared, with the exception of that of europium which could not be obtained, and their melting points determined.[41] Europium di- and tri-halides have been examined.[42] Argento- and auro-cyanides are formed by the tervalent rare-earth metals of the cerium group.[43]

Sodium cericarbonate, $Na_6[Ce(CO_3)_5],12H_2O$, has been obtained in the form of yellow prismatic crystals isomorphous with the corresponding thorium salt.[44]

Details have been given of the separation of yttrium of high purity by the fractional crystallisation of the double carbonates of the yttria-earth elements and sodium, followed by a fractional precipitation of the crystalline double ferrocyanides with the alkali metals in presence of a large excess of the alkali-metal salt. The object of the ferrocyanide treatment is to remove a small amount of erbium.[45]

Group IV.

By an application of the Nernst heat theorem it is found that from $0°$ to $1100°$ Abs. graphite is more stable than diamond, whilst the dimorphism is truly monotropic and not pseudo-monotropic. The heat of transition changes sign at $850°$ Abs., above which temperature diamond changes into graphite with absorption of heat.[46] The position of the equilibrium $C + CO_2 \rightleftharpoons 2CO$ depends on the character of the carbon and its pre-treatment.[47] The double carbonates $Na_2CO_3,MgCO_3$ and $Na_2CO_3,CaCO_3$ and the corresponding potassium compounds have been prepared, but attempts to make dolomite were unsuccessful.[48] Carbon sulphidoselenide is formed by the action of carbon disulphide vapour on ferrous selenide at $650°$; several of its physical and chemical properties have been determined.[49] Complex cyanates of a number of heavy metals and containing hexamethylenetetramine have been prepared; they are of the general formula $[X(H_2O)_2,C_6H_{12}N_4](CNO)_2$ and are more stable and less soluble than the simple cyanates.[50]

[41] G. Jantsch, H. Grubitsch, F. Hoffmann, and H. Alber, *Z. anorg. Chem.*, 1929, **185**, 49.

[42] G. Jantsch, H. Alber, and H. Grubitsch, *Monatsh.*, 1929, **53** and **54**, 305; *A.*, 1407.

[43] G. A. Barbieri, *Atti R. Accad. Lincei*, 1929, [vi], **9**, 906; *A.*, 1026.

[44] L. Lortie, *Compt. rend.*, 1929, **188**, 915; *A.*, 524.

[45] G. Canneri, *Atti R. Accad. Lincei*, 1929, [vi], **8**, 164; *A.*, 158.

[46] N. Nagasako, *Bull. Chem. Soc. Japan*, 1928, **3**, 209; *A.*, 20.

[47] F. J. Dent and J. W. Cobb, *J.*, 1929, 1903; *A.*, 1237.

[48] W. Eitel and W. Skaliks, *Naturwiss.*, 1929, **17**, 316; *A.*, 777.

[49] H. V. A. Briscoe, J. B. Peel, and P. L. Robinson, *J.*, 1929, 56, 1048; *A.*, 410, 778.

[50] R. Ripan, *Bul. Soc. Stiinte Cluj*, 1928, **4**, 29; *Chem. Zentr.*, 1928, 2938; *A.*, 41.

The partial solubility of silicon in hydrofluoric acid under certain conditions appears to be due to oxidation.[51] The stability regions of the several forms of silica have been re-investigated [52] and the results of Fenner [53] confirmed.

A number of important slag equilibria have been studied, namely, those between ferrous sulphide and lead, cuprous, and nickel silicates, and several similar ones.[54]

By the action of silicon tetrachloride vapour on water, with careful attention to the acidity, it has been found possible to prepare solutions of nearly pure mono- and di-silicic acid.[55] $SiO_2,2H_2O$ was obtained by hydrolysis of ethyl orthosilicate at ordinary temperature, and from it $2SiO_2,3H_2O$ and $(SiO_2,H_2O)_x$ were obtained by desiccation at $13°$.[56] According to R. Schwarz and H. Richter,[57] the gel produced by hydrolysis of silicon tetrachloride by water at $0°$, followed by thorough washing and drying with acetone below $2°$, has a composition very close to that of a metasilicic acid, $(SiO_2,H_2O)_x$. Titanium tetrachloride similarly treated yields $TiO_2,2H_2O$. A silicic acid prepared, in absence of water, by the action of silicon tetrachloride on triphenylcarbinol dissolved in anhydrous ether also had a water content very close to that of the meta-acid.[58] Titanium sesquioxide and ferrous oxide heated together to $1000°$ yield a spinel.[59] A number of compounds of titanium tetra-chloride and -bromide with cyanogen bromide or hydrocyanic acid have been isolated.[60] Zirconium iodide has been prepared.[61] Zirconium oxide gels age very slowly, and the process seems to end with ZrO_2 without indication of any definite intermediate hydrated compound.[62]

R. Schwarz and H. Giese [63] have examined the peroxides of titanium, zirconium, hafnium, and thorium; those of the first three metals behave as peroxy-ortho-acids of the general formula

[51] C. Bedel, *Compt. rend.*, 1929, **188**, 1255; **189**, 180; *A.*, 756, 997; A. Sanfourche, *ibid.*, **188**, 1672; **189**, 533; *A.*, 1030, 1251.

[52] C. J. van Nieuwenburg, *Rec. trav. chim.*, 1929, **48**, 402; *A.*, 637.

[53] *A.*, 1913, ii, 133.

[54] W. Jander and K. Rothschild, *Metall-Wirtschaft*, 1928, **7**, 580; *Chem. Zentr.*, 1928, i, 2897; *A.*, 31.

[55] R. Willstätter, H. Kraut, and K. Lobinger, *Ber.*, 1928, **61**, [B], 2280; 1929, **62**, [B], 2027; *A.*, 39, 1251.

[56] P. A. Thiessen and O. Koerner, *Z. anorg. Chem.*, 1929, **182**, 343; *A.*, 1154.

[57] *Ber.*, 1929, **62**, [B], 31; *A.*, 280.

[58] W. Dilthey and E. Hölterhoff, *ibid.*, p. 24; *A.*, 280.

[59] F. Halla, *Z. anorg. Chem.*, 1929, **184**, 421.

[60] F. Oberhauser and J. Schormüller, *Ber.*, 1929, **62**, [B], 1436; *A.*, 896.

[61] E. Chauvenet and J. Davidowicz, *Compt. rend.*, 1929, **189**, 408; *A.*, 1154.

[62] A. Simon and O. Fischer, *Z. anorg. Chem.*, 1929, **185**, 130.

[63] *Ibid.*, 1928, **176**, 209; *A.*, 39.

$M(OOH)(OH)_3$, whilst that of thorium is $Th_2O_7,4H_2O$. Potassium pertitanate and perzirconate are found to be $K_4TiO_8,6H_2O$ and $K_4ZrO_8,6H_2O$ and are regarded as salts of tetraperoxy-ortho-acids. The conditions necessary to precipitate zirconium completely as phosphate have been examined.[64] The compounds

$$Th(HPO_4)(H_2PO_4)_2,2H_2O,$$
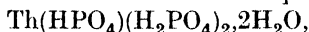
$Th(SO_4)(HPO_4),4H_2O$, and $Th_2(SO_4)(H_2PO_4)_6,8H_2O$ have been obtained by J. D'Ans and W. Dawihl.[65]

Full details of the preparation of pure germanium dioxide from germanite and its conversion into the tetrachloride have been published by L. Dede and W. Russ [66] and by W. Pugh,[67] and C. James and H. C. Fogg [68] obtained a rapid concentration of the germanium and gallium contained in certain samples of zinc oxide in a simple manner : a solution of the zinc oxide in hydrochloric acid is rendered basic by the slow addition of some of the original zinc oxide, the mixture is filtered, the residue containing the germanium and gallium is dissolved in acid, and the solution is distilled and treated in the usual manner to obtain the two elements. The solubility of germanium dioxide in hydrochloric and sulphuric acids of various concentrations has been measured. There is no evidence for the formation of a germanium sulphate, for the solubility falls continuously with increasing concentration of the sulphuric acid, but with hydrochloric acid the solubility passes through a minimum in 5·3N-acid and thereafter increases owing to formation of tetrachloride. Except in very strongly acid solutions, the germanium dioxide behaves essentially as an acid oxide.[69] W. Pugh [70] has also studied the hydrolysis of sodium germanate and has determined the first and second dissociation constants of germanic acid to be $2\cdot6 \times 10^{-9}$ and $1\cdot9 \times 10^{-13}$ respectively. Germanic acid and several germanates have also been examined by R. Schwarz.[71]

L. M. Dennis and H. L. Hunter [72] have at last succeeded in preparing germanium dichloride by the action of the vapour of the tetrachloride on metallic germanium at 350°; it is a light yellow solid with properties very similar to those of the dibromide.[73] GeH_3Cl, GeH_2Cl_2, GeH_3Br, and GeH_2Br_2 have all been obtained by the action of hydrochloric or hydrobromic acid on GeH_4 in presence

[64] R. D. Reed and J. R. Withrow, *J. Amer. Chem. Soc.*, 1929, **51**, 1311; *A.*, 778.

[65] *Z. anorg. Chem.*, 1929, **178**, 252; *A.*, 411.

[66] *Ber.*, 1928, **61**, [*B*], 2451; *A.*, 158.   [67] *J.*, 1929, 2540; *A.*, 1930, 47.

[68] *J. Amer. Chem. Soc.*, 1929, **51**, 1459; *A.*, 778.

[69] W. Pugh, *J.*, 1929, 1537; *A.*, 997.   [70] *Ibid.*, p. 1994; *A.*, 1237.

[71] *Ber.*, 1929, **62**, [*B*], 2477; *A.*, 1407.

[72] *J. Amer. Chem. Soc.*, 1929, **51**, 1151; *A.*, 662.

[73] *Ann. Reports*, 1928, **25**, 53.

of anhydrous aluminium chloride or bromide, and their properties are described.[74]

By studying the change in the diffusion coefficient of the stannate ion caused by the gradual addition of acid to strongly alkaline stannate solutions, and also the change in the ultra-violet absorption, it is concluded that a change occurs in such solutions which is not simply the change from a normal to an acid stannate

$$Na_2[Sn(OH)_6] + HCl = NaH[Sn(OH)_6] + NaCl,$$
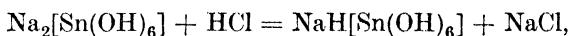
but is much more comparable with the conversion of a chromate into a dichromate and is representable by an equation such as

$$2[Sn(OH)_6]'' + 2H^{\cdot} \rightleftharpoons [Sn_2(OH)_{10}]'' + 2H_2O.[75]$$
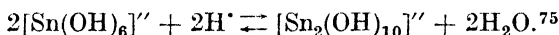
The concentration of chlorine ions and hydrogen ions in aqueous stannic chloride solutions has been determined. In dilute solutions these are equal, but in solutions of concentrations greater than $0.1M$ an excess of chlorine ions is present. Complete inhibition of hydrolysis does not take place even in presence of $4N$-hydrochloric acid.[76] A number of complex amminated stannibromides of various heavy metals have been prepared by G. Spacu and J. Dick.[77]

The dissolution of lead and cadmium in their respective fused chlorides is a chemical process involving the formation of a lower chloride.[78] $(PbCl)_2CO_3$, identical with the mineral phosgenite, is said to be precipitated as an intermediate stage in the action of sodium carbonate on lead chloride solution.[79] Lead nitrate forms with ammonia a hexammine, a triammine, and a monoammine; lead sulphate yields a tetrammine and a diammine.[80]

The equilibrium $PbS + H_2 \rightleftharpoons Pb + H_2S$ has been investigated at various temperatures between $655°$ and $1000°$.[81]

Since sodium plumbate, $Na_2PbO_3,3H_2O$, loses all its water simultaneously at $110°$ without any liberation of oxygen, it must be derived from metaplumbic acid and does not possess the formula $Na_2[Pb(OH)_6]$.[82]

Group V.

The nature of active nitrogen and the cause of its after-glow are still obscure. The knowledge with respect to the subject was

[74] L. M. Dennis and P. R. Judy, *J. Amer. Chem. Soc.*, 1929, **51**, 2321; *A.*, 1154.

[75] G. Jander, F. Busch, and T. Aden, *Z. anorg. Chem.*, 1928, **177**, 345; *A.*, 281.

[76] L. Smith and A. Persson, *ibid.*, **176**, 155; *A.*, 29.

[77] *Bul. Soc. Stiinte Cluj*, 1928, **4**, 84, 110; *Chem. Zentr.*, 1928, ii, 1196; *A.*, 281.

[78] W. Eitel and B. Lange, *Z. anorg. Chem.*, 1929, **178**, 108; *A.*, 411.

[79] (Mme.) N. Demassieux, *Compt. rend.*, 1929, **189**, 333; *A.*, 1154.

[80] W. Krings, *Z. anorg. Chem.*, 1929, **181**, 309; *A.*, 1026.

[81] K. Jellinek and A. Deubel, *Z. Elektrochem.*, 1929, **35**, 451; *A.*, 1012.

[82] A. Simon, *Z. anorg. Chem.*, 1928, **177**, 109; *A.*, 158.

summarised by C. N. Hinshelwood.[83] The rate of decay of the after-glow and the influence of the walls of the containing vessel upon this have been investigated, as also the effect of small additions of other substances.[84] It appears to be necessary to assume the presence of nitrogen atoms, and possibly of metastable molecules too, in order to explain the results, although, according to some authors, no appreciable density of atoms is present.[85] Z. Bay and W. Steiner [86] state that active nitrogen generally consists of a mixture of ordinary and metastable (8-volt) nitrogen molecules with ordinary and metastable (2·37- and 3·56-volt) nitrogen atoms, and its properties depend upon the mixture ratio. The presence of atoms is essential for the after-glow. Active nitrogen, apart from complications due to the nature of the walls, is not properly described unless the conditions of excitation are accurately specified. Nitrogen activated by the dark electric discharge unites with the alkali metals to produce azides with some secondary nitride.[87] Such nitrogen also readily combines with sulphur at 80—100° to yield a mixture of several nitrogen sulphides.[88] When an arc is struck in nitrogen between iron electrodes considerable formation of iron nitride, Fe_4N_2, occurs.[89]

The (reversible) decomposition pressures of boron nitride have been determined between 1695° and 2045°, and some other nitrides examined at high temperatures.[90]

No evidence in support of the suggested existence of active and inactive phases of ammonia could be found by W. H. Stringfellow.[91] Vapour-density measurements have shown that the vapours of (moist) ammonium chloride, bromide, and iodide are completely dissociated even in presence of the solid salt.[92] Intensively dried ammonium chloride also dissociates completely on vaporisation.[93]

[83] *Nature*, 1928, **122**, 404; *A.*, 39.

[84] H. O. Kneser, *Ann. Physik.*, 1928, [iv], **87**, 717; *Physikal. Z.*, 1928, **29**, 895; *A.*, 6; B. Lewis, *J. Amer. Chem. Soc.*, 1929, **51**, 654, 665; *A.*, 624; E. J. B. Willey, *Nature*, 1929, **124**, 443; *A.*, 1117.

[85] P. K. Kichlu and S. Basu, *ibid.*, **123**, 715; *A.*, 624; P. K. Kichlu and D. P. Acharya, *Proc. Roy. Soc.*, 1929, [A], **123**, 168; *A.*, 624, but see Lord Rayleigh, *Nature*, 1929, **123**, 716; *A.*, 624.

[86] *Naturwiss.*, 1929, **17**, 442; *A.*, 863; *Z. Elektrochem.*, 1929, **35**, 733; *A.*, 1359.

[87] W. Moldenhauer and H. Möttig, *Ber.*, 1929, **62**, [B], 1954; *A.*, 1247.

[88] W. Moldenhauer and A. Zimmermann, *ibid.*, p. 2390; *A.*, 1252.

[89] E. J. B. Willey, *J.*, 1928, 2840; *A.*, 39.

[90] R. Lorenz and J. Woolcock, *Z. anorg. Chem.*, 1928, **176**, 289; *A.*, 29.

[91] *J.*, 1929, 1; *A.*, 281.

[92] A. Smits and R. Purcell, *J.*, 1928, 2936; *A.*, 128; A. Smits and W. de Lange, *ibid.*, p. 2944; *A.*, 128; R. H. Purcell and W. de Lange, *J.*, 1929, 275; *A.*, 387.

[93] W. H. Rodebush and J. C. Michalek, *J. Amer. Chem. Soc.*, 1929, **51**, 748; *A.*, 636.

The ternary system NH_3–CO_2–H_2O has been studied at temperatures above 60°, steel bombs being used for reaction vessels. In the neighbourhood of 80—100° a double compound of ammonium hydrogen carbonate and ammonium carbamate is formed, but this does not exist above 106°, which is the m. p. of ammonium hydrogen carbonate. Above 135° all these compounds are unstable and are converted into carbamide. A space diagram of the ternary system is given.[94]

The conditions under which monobromoamine can be produced by the action of bromine on ammonia have been examined; unlike monochloroamine it does not yield hydrazine with ammonia.[95] The influence of various factors on the interaction of monochloroamine with ammonia have been studied. Very small amounts of cupric, ferrous, and cobaltous ions decrease the amount of hydrazine formed. The favourable influence of mannitol and gelatin on the yield of hydrazine is attributed to adsorption of these ions by the gelatin or mannitol.[96] Chlorination of excess of ammonium ions at the ordinary temperature yields only NH_2Cl when the p_H of the solution exceeds 8·5, practically only $NHCl_2$ when the p_H is between 4·5 and 5·0, and NCl_3 when the p_H is below 4·4.[97] A method of concentrating hydrazine hydrate solutions by distillation with xylene has been described.[98]

The conditions have been given under which azoimide and its salts can be safely and conveniently prepared.[99] Molecular hydrogen in presence of colloidal palladium has a very slight reducing action on azoimide in alkaline solution, but in acid solution reduction to ammonia and hydrazine is complete. Nascent hydrogen from zinc or iron and hydrochloric acid gives the same result.[1]

According to K. Gleu and E. Roell,[2] when oxygen containing 10% of ozone is passed into a N-sodium azide solution an unstable orange substance is produced which reacts quantitatively as a pernitrous acid, isomeric with nitric acid and having the structure $O\colon N\cdot O\cdot OH$. In a mixed chloroform–carbon tetrachloride solution three reactions occur when nitrogen trichloride reacts with nitric oxide at temperatures between 0° and − 80°; these can be represented by the equations (a) $2NCl_3 = N_2 + 3Cl_2$; (b) $NOCl + NCl_3 = N_2O +$

[94] E. Terres and H. Behrens, *Z. physikal. Chem.*, 1928, **139**, 695; *A.*, 141; see also E. Jänecke, *Z. Elektrochem.*, 1929, **35**, 716; *A.*, 1388.

[95] W. Moldenhauer and M. Burger, *Ber.*, 1929, **62**, [*B*], 1615; *A.*, 897.

[96] M. Bodenstein and Titschack, *Z. physikal. Chem.*, 1928, **139**, 397; *A.*, 282.

[97] R. M. Chapin, *J. Amer. Chem. Soc.*, 1929, **51**, 2112; *A.*, 1026.

[98] C. D. Hurd and C. W. Bennett, *ibid.*, p. 265; *A.*, 282.

[99] W. Hoth and G. Pyl, *Z. angew. Chem.*, 1929, **42**, 888; *A.*, 1155.

[1] B. Ricca and F. Pirrone, *Gazzetta*, 1929, **59**, 379; *A.*, 1150.

[2] *Z. anorg. Chem.*, 1929, **179**, 233; *A.*, 523.

$2Cl_2$; (c) $NCl_3 + 2NO = N_2O + NOCl + Cl_2$. Reaction (a) is catalysed by the nitric oxide.[3]

When hydroxylamine is prepared by electrolytic reduction of nitric acid in sulphuric acid solution, a mercury cathode being used, considerable quantities of hydroxylamine*iso*monosulphonic acid are also formed ; the influence of various factors on the yield of hydroxylamine has been examined.[4] L. Cambi has examined the decomposition of hyponitrous acid under various conditions.[5] The combination of nitric oxide with oxygen to form nitrogen peroxide follows a termolecular course.[6] The conditions which influence the interaction of nitric oxide and hydrogen sulphide to form water, sulphur, and nitrogen have been investigated,[7] and so has the equilibrium between nitrogen trioxide and its dissociation products, nitric oxide and peroxide.[8]

Nitrogen peroxide and sulphur dioxide react in the liquid state according to the scheme $1\cdot5N_2O_4 + 2SO_2 = S_2N_2O_9 + NO$. $S_2N_2O_9$ is a white crystalline solid with the properties of an anhydride of nitrosylsulphuric acid.[9] A substance of the same composition has been prepared by methods which suggest that it has the structure $NO\cdot O\cdot SO_2\cdot O\cdot SO_2\cdot ONO$, but the similar compound $SO_2(O\cdot NO)_2$ could not be isolated.[10] Pure nitryl chloride, NO_2Cl, has been prepared [11] by treatment of gaseous nitrosyl chloride with ozone, cooling the product in liquid air, and removing the oxygen formed according to the equation $NOCl + O_3 = NO_2Cl + O_2$; it is a colourless gas which condenses at $-15°$ to a colourless liquid of $d^{0\cdot}$ $1\cdot37$ and f. p. $-145°$.

Nitrogen sulphide, N_4S_4, in benzene is converted by stannous chloride in 96% alcohol into $(HSN)_4$. From the reactions of this compound, its structure is considered to be $N\!\!<^{SH=N-SH}_{SH-N=SH}\!\!>N$, whilst N_4S_4 is $N\!\!<^{S=N-S}_{S-N=S}\!\!>N$.[12]

[3] W. A. Noyes, *J. Amer. Chem. Soc.*, 1928, **50**, 2902; *A.*, 158.

[4] J. G. Stscherbakov and D. M. Libina, *Z. Elektrochem.*, 1929, **35**, 70; *A.*, 274.

[5] *Gazzetta*, 1929, **59**, 770.

[6] (Frl.) G. Kornfeld and E. Klingler, *Z. physikal. Chem.*, 1929, [B], **4**, 37; *A.*, 887.

[7] J. Pierce, *J. Physical Chem.*, 1929, **33**, 22; *A.*, 281.

[8] E. Abel and J. Proisl, *Z. Elektrochem.*, 1929, **35**, 712; *A.*, 1383.

[9] E. Briner, G. H. Lunge, and A. van der Wijk, *Helv. Chim. Acta*, 1928, **11**, 1125; *A.*, 40; W. Manchot and H. Schmid, *Ber.*, 1929, **62**, [B], 1261; *A.*, 779.

[10] C. W. H. Jones, W. J. Price, and H. W. Webb, *J.*, 1929, 312; *A.*, 411.

[11] H. J. Schumacher and J. Sprenger, *Z. anorg. Chem.*, 1929, **182**, 139; *A.*, 1155; *Z. Elektrochem.*, 1929, **35**, 653; *A.*, 1395.

[12] A. Meuwsen, *Ber.*, 1929, **62**, [B], 1959; *A.*, 1252.

A number of chlorobromides of phosphorus are stated to be formed by the action of bromine on phosphorus trichloride or its vapour,[13] whereas the pentachloride is said to yield with bromine the reddish-brown compound $PCl_5,5Br_2$, melting at $25°$ with decomposition.[14]

The investigations of A. Petrikaln [15] on the emission and absorption spectra of phosphorus pentoxide and phosphorus trioxide indicate that the band spectrum in the phosphorus luminescence spectrum is due to phosphorus trioxide while the continuous spectrum is due to the pentoxide. The precautions needed in the preparation of phosphorus oxide so as to obtain a product containing the minimum amount of yellow phosphorus are described by L. Wolf and H. Schmager [16]; further papers dealing with the removal of these traces of yellow phosphorus have been published.[17]

Phosphorus trioxide cannot be prepared by the action of the trichloride on phosphorous acid or on acetic anhydride or glacial acetic acid.[18] Pure sublimed phosphorus pentoxide rapidly absorbs appreciable amounts of intensively dried ammonia, forming a protective film on the pentoxide.[19] Dichlorophosphoric acid is formed as a recognisable intermediate stage in the action of ice-cold water on phosphoryl chloride or phosphorus pentachloride.[20] Difluorophosphoric acid, HPO_2F_2, is produced [21] when phosphoryl fluoride is hydrolysed by cold dilute alkali hydroxide and is conveniently isolated as the nitron salt. The ammonium salt is obtained by heating phosphoric oxide with 3 mols. of ammonium fluoride in a copper or nickel crucible at $135°$ and extracting the cold product with alcohol. Many other difluorophosphates have been prepared by double decomposition from the ammonium salt. Difluorophosphoric acid resembles perchloric acid to a small extent; when it is boiled with very dilute potassium hydroxide, monofluorophosphate is formed and can be isolated as the silver salt, Ag_2PO_3F, from which other salts can be prepared. These salts show analogies with the sulphates and are very stable in neutral or alkaline solution

[13] T. Miłobędzki and S. Krakowiecki, *Rocz. Chem.*, 1928, **8**, 563; *A.*, 411.

[14] W. A. Plotnikov and S. I. Jakubson, *Z. physikal. Chem.*, 1928, **138**, 243; *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1513; *A.*, 158, 663.

[15] *Z. Physik*, 1928, **51**, 395; *A.*, 377.

[16] *Ber.*, 1929, **62**, [*B*], 771; *A.*, 662.

[17] (Miss) C. C. Miller, *J.*, 1929, 1823, 1829; *A.*, 1155; *Ann. Reports*, 1928, **25**, 56.

[18] L. Wolf, E. Kalaehne, and H. Schmager, *Ber.*, 1929, **62**, [*B*], 1441; *A.*, 897; W. P. Jorissen and A. Tasman, *Rec. trav. chim.*, 1929, **48**, 324; *A.*, 662.

[19] L. Harris and C. B. Wooster, *J. Amer. Chem. Soc.*, 1929, **51**, 2121; *A.* 1154.

[20] H. Meerwein and K. Bodendorf, *Ber.*, 1929, **62**, [*B*], 1952; *A.*, 1252.

[21] W. Lange, *ibid.*, pp. 786, 793; *A.*, 662.

but are rapidly decomposed in hot acid solution. It has been established that there exists a definite equilibrium $H_3PO_4 + HF \rightleftharpoons H_2PO_3F + H_2O$.[22] The preparation of a number of crystalline phosphates and arsenates (of Mn, Co, Ni, Cu, and Cd) has been described by F. Ephraim and C. Rossetti.[23] Hypophosphoric acid can be prepared in good yield by the oxidation of red phosphorus with alkaline permanganate, or peroxide, or hypochlorite.[24] From the fact that the hydrolysis of the acid follows a unimolecular course, it is concluded that it is $H_4P_2O_6$ and not H_2PO_3.[25]

Silicophosphoric acid, $H_8Si(PO_4)_4$, is extremely unstable, but thermal analysis of the system $Na_2O-SiO_2-P_2O_5$ indicates the existence of the sodium salt melting at $961°$.[26] The solubilities of arsenic tri- and penta-sulphides in pure water and in hydrogen sulphide solutions at $0°$ have been determined, and the bearing of the results on precipitations of arsenic as sulphide for analytical purposes has been discussed.[27] An elaborate investigation of the thioarsenites of sodium, potassium, ammonium, calcium, strontium, and barium has been made by H. Wünschendorff.[28] In addition to salts of the ortho-, pyro-, and meta-acids, others containing a still higher proportion of As_2S_3, such as $K_2As_4S_7,2H_2O$ and $K_2As_6S_{10},3H_2O$, could be prepared in some cases. There is always a tendency for the solutions from which these compounds are formed to decompose into metallic arsenic and thioarsenate, and this prevents the preparation of certain members of the series such as K_3AsS_3 and $K_4As_2S_5$. The compounds described are crystalline. Finely divided antimony is soluble in distilled water in the presence of oxygen, and this may be a source of error in any analytical method where deposits of antimony have to be washed.[29] In the presence of a relatively strong acid, the orthosulphovanadates, R_3VS_4, give V_2S_5, but in the presence of hydrogen sulphide they give RVS_3 and $R_4[H_2(VS_3)_6]$. This has been confirmed by the preparation of the compounds $NH_4VS_3,2H_2O$ and
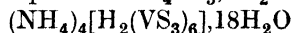
$$(NH_4)_4[H_2(VS_3)_6],18H_2O$$

by the action of ammonium hydrosulphide and hydrogen sulphide on the orthovanadate. The corresponding guanidine salts and $Tl_4[H_2(VS_3)_6],18H_2O$ were prepared from the ammonium salts by

[22] W. Lange,, *Ber.*, 1929, **62**, [*B*], 1084; *A.*, 764.

[23] *Helv. Chim. Acta*, 1929, **12**, 1025; *A.*, 1930, 47.

[24] F. Vogel, *Z. angew. Chem.*, 1929, **42**, 263; *A.*, 525; J. Probst, *Z. anorg. Chem.*, 1929, **179**, 155; *A.*, 525.

[25] A. Rosenheim and H. Zilg, *Z. physikal. Chem.*, 1928, **139**, 12; *A.*, 148.

[26] R. Schwarz, *Z. anorg. Chem.*, 1928, **176**, 236; *A.*, 39.

[27] R. Höltje, *ibid.*, 1929, **181**, 395; *A.*, 997.

[28] *Bull. Soc. chim.*, 1929, [iv], **45**, 889, 897, 903; *A.*, 1930, 48.

[29] J. Grant, *Analyst*, 1929, **54**, 227; *A.*, 639.

double decomposition.[30]   Other complex sulpho-salts of vanadium (and a few of molybdenum) of different types from the above are described by the same authors.[31]   Tantalum pentabromide is prepared by distilling bromine on to powdered tantalum heated to 260—300° in an atmosphere of nitrogen or argon.[32]   The behaviour of a number of tantalum compounds under various conditions is described in a paper by V. Spitzin and L. Kaschtanov.[33]

Group VI.

The kinetics of the formation of ozone by the action of cathode rays and by electrical discharges have been studied,[34] and also the thermal decomposition of ozone at low pressures.[35]   The influence of cathode rays on the union of hydrogen and oxygen and on various gases such as oxygen, nitric oxide, and carbon dioxide has also been investigated.[36]   Full details have been published by K. F. Bonhoeffer and H. Reichardt of work which showed the formation of free hydroxyl at temperatures above 1300° : [37] it is also formed in water-vapour discharge tubes.[38]

The behaviour of pure hydrogen peroxide with a number of compounds is recorded, together with the f. p. curves of some binary hydrogen peroxide systems.[39]   A number of sodium and potassium phosphates containing hydrogen peroxide of crystallisation have been prepared.   They differ from true perphosphates prepared electrolytically inasmuch as ether extracts the hydrogen peroxide, which is also evolved at 130° in a vacuum.[40]

Sulphur tetrafluoride has been prepared, by the action of cobaltic fluoride on sulphur at 120°, as a colourless reactive gas condensing at − 40° and 1 atm. pressure to a clear mobile liquid.[41]   There is still some doubt about the nature of the liquid mixtures of sulphur

[30] L. Fernandes and C. Orlandi, *Atti R. Accad. Lincei*, 1928, [vi], **8**, 234; *A.*, 525.

[31] *Idem, ibid.*, 1929, [vi], **9**, 409; *A.*, 663.

[32] K. R. Krishnaswami, *Nature*, 1928, **122**, 845; *A.*, 40.

[33] *Z. anorg. Chem.*, 1929, **182**, 207; *A.*, 1253.

[34] A. L. Marshall, *J. Amer. Chem. Soc.*, 1928, **50**, 3178; *A.*, 155; J. K. Hunt, *ibid.*, 1929, **51**, 30; *A.*, 274.

[35] E. H. Riesenfeld and H. J. Schumacher, *Z. physikal. Chem.*, 1928, **138**, 268; *A.*, 146; E. H. Riesenfeld and E. Wassmuth, *ibid.*, 1929, **143**, 397; *A.*, 1242.

[36] A. L. Marshall, *J. Amer. Chem. Soc.*, 1928, **50**, 3197; *A.*, 155; W. F. Busse and F. Daniels, *ibid.*, p. 3271; *A.*, 155.

[37] *Z. physikal. Chem.*, 1928, **139**, 75; *A.*, 396; *Ann. Reports*, 1928, **25**, 341.

[38] G. I. Lavin and F. B. Stewart, *Nature*, 1929, **123**, 607; *A.*, 520.

[39] G. L. Matheson and O. Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 674; *A.*, 523.

[40] H. Menzel and G. Gäbler, *Z. anorg. Chem.*, 1928, **177**, 187; *A.*, 278.

[41] J. Fischer and W. Jaenckner, *Z. angew. Chem.*, 1929, **42**, 810; *A.*, 1155.

chlorides, in spite of a good deal of work on the subject, but there seems no doubt that three definite compounds exist, $viz.$, S_2Cl_2, SCl_2, and SCl_4.[42]

$SbCl_5,SCl_4$ is formed by the action of sulphur monochloride on antimony pentachloride, but no evidence could be obtained for the existence of the compound $2AsCl_3,3SCl_2$ given in the literature.[43]

The action of carbon tetrabromide on sulphur and on selenium has been examined. S_2Br_2, Se_2Br_2, and $SeBr_4$ are formed among other products.[44] Heating a mixture of paraffin (25 g.), sulphur (15 g.), and asbestos (5 g.) is recommended as a convenient way of preparing hydrogen sulphide.[45] The action of hydrogen sulphide on nitric acid and on solutions of potassium chromate has been investigated.[46]

Electrolysis of sodium sulphide solutions yields only polysulphide at low current densities; dithionate and sulphate are formed at higher current densities, but no thiosulphate.[47] Crystalline compounds of the type $M_4[Fe(CN)_5NOS]$ have been obtained by the interaction of the alkali-metal sulphides with sodium nitroprusside in absolute methyl alcohol.[48]

Sodium and potassium sulphites in aqueous solution are oxidised to dithionates when warmed with lead dioxide, which is reduced to triplumbic tetroxide; manganese dioxide does not react.[49] D. Vorländer and A. Lainau [50] have made a thorough study of the oxidation of ammonium sulphite to ammonium sulphate by air, the effect of various alterations in conditions and of various catalysts being examined.

Tri-substituted derivatives of aminosulphonic acid, $NR_3 \cdot SO_2 \cdot O$,

form neutral solutions in water without immediately suffering hydrolysis. Alkali decomposes them more readily, usually into tertiary amine and sulphate. With acids they can form salts and complex compounds such as $[NMe_3,SO_3H]ClO_4,H_2O$ and $[NMe_3,SO_3]_2KI,I_5,2H_2O$. Solid aminosulphonic acid probably has a betaine structure, which would be more in keeping with its high

[42] M. Trautz, (Frl.) H. Acker, L. E. von Broecker, A. Rick, A. Hoffmann, H. Klippel, and O. Loth, $Z.$ $Elektrochem.$, 1929, **35**, 110; $A.$, 525; T. M. Lowry and G. Jessop, $J.$, 1929, 1421; $A.$, 978.

[43] J. R. Partington, $ibid.$, pp. 2573, 2577; $A.$, 1930, 48.

[44] H. V. A. Briscoe, J. B. Peel, and J. R. Rowlands, $ibid.$, p. 1766; $A.$, 1155.

[45] H. Gfeller and K. Schaefer, $Schweiz.$ $Apoth.-Ztg.$, 1929, **67**, 109; $A.$, 1253.

[46] H. B. Dunnicliff and S. Mohammad, $J.$ $Physical$ $Chem.$, 1929, **33**, 1343; $A.$, 1253; H. B. Dunnicliff and C. L. Soni, $ibid.$, p. 81; $A.$, 282.

[47] W. R. Fetzer, $J.$ $Physical$ $Chem.$, 1928, **32**, 1787; $A.$, 154.

[48] G. Scagliarini and P. Pratesi, $Atti$ $R.$ $Accad$ $Lincei$, 1928, [vi], **8**, 75; $A.$, 160.

[49] R. Hac, $J.$ $Czech.$ $Chem.$ $Comm.$, 1929, **1**, 259; $A.$, 777.

[50] $J.$ $pr.$ $Chem.$, 1929, **123**, 351; $A.$, 1930, 41.

m. p., non-hygroscopic character, and limited solubility than the formula $NH_2 \cdot SO_2 \cdot OH$ usually assigned to it.[51]

The rate of decomposition of sodium and potassium persulphates under a great variety of conditions has been examined : a unimolecular course is followed fairly closely.[52]

F. Foerster [53] continues his investigations of the sulphur acids, which he still interprets in terms of the hypothetical SO. The latter compound also plays an important part in the decomposition of thiosulphate by acid according to O. von Deines,[54] who states that hydrogen persulphide is also produced. Some work on the mechanism of the decomposition of thiosulphuric acid has been carried out by J. Scheffer and F. Böhm.[55]

The formation of thiosulphate by hydrolysis of trithionate has been demonstrated by adding potassium trithionate to a cold saturated solution of copper acetate, whereupon the double potassium cuprous thiosulphate, $K_2S_2O_3, Cu_2S_2O_3, 2H_2O$, separated in a few days.[56] The existence of potassium hexathionate has been confirmed by J. R. Partington and A. F. Tipler.[57] Six-membered ring formulæ have been proposed for tetra- and penta-thionic acids, but seem improbable as they contain peroxidic oxygen.[58]

A number of amminated selenocyanates of heavy metals have been prepared.[59] The oxide formed by the action of ozone on selenium dissolved in $SeOCl_2$ is found to be selenium dioxide.[60] By the action of hydrogen chloride on selenium dioxide two compounds are formed, viz., $SeO_2, 4HCl$, a yellow solid, and $SeO_2, 2HCl$, a yellow liquid.[61] Various methods of preparing selenic and telluric acids from the dioxides by oxidation have been described.[62] H. D. K. Drew [63] has shown that Vernon's [64] two forms of dimethyltelluron-

[51] P. Baumgarten, *Ber.*, 1929, **62**, [*B*], 820; *A.*, 663.

[52] A. Kailan and E. Leisek, *Monatsh.*, 1928, **50**, 403; *A.*, 148.

[53] F. Foerster, E. Haufe, and E. Kircheisen, *Z. anorg. Chem.*, 1928, **177**, 17, 42, 61; *A.*, 159.

[54] *Ibid.*, p. 13; *A.*, 159.

[55] *Ibid.*, 1929, **183**, 151; *A.*, 1253.

[56] A. Hornig, *ibid.*, 1928, **176**, 423; *A.*, 40.

[57] *J.*, 1929, 1382; *A.*, 896; *Ann. Reports*, 1928, **25**, 58.

[58] J. A. Christiansen, *Förh. III nord. Kemistmötet*, 1928, 177; *A.*, 122.

[59] G. Spacu and R. Ripan, *Bul. Soc. Stiinte Cluj*, 1928, **4**, 3; *Chem. Zentr.*, 1928, i, 2937; *A.*, 41.

[60] G. F. Hoffmann and V. Lenher, *J. Amer. Chem. Soc.*, 1929, **51**, 3177; *A.*, 1930, 48.

[61] T. W. Parker and P. L. Robinson, *J.*, 1928, 2853; *A.*, 40.

[62] E. R. Huff and C. R. McCrosky, *J. Amer. Chem. Soc.*, 1929, **51**, 1457; *A.*, 799; F. C. Mathers and F. V. Graham, *ibid.*, p. 225; *A.*, 1930, 48; F. C. Mathers and G. M. Bradbury, *ibid.*, p. 3229; *A.*, 1930, 48.

[63] *J.*, 1929, 560; *A.*, 546.

[64] *J.*, 1920, **117**, 86, 897; 1921, **119**, 105, 687.

ium di-iodide and dibromide are not stereoisomerides as the latter supposed. Halides of the α-series are normal in type, non-polar, and have a tellurium atom with a tetrahedral valency distribution. The compounds of the β-series are salt-like complex substances of the same empirical formulæ as the corresponding substances in the α-series, with the probable constitution $[Me_3Te]^+[TeMeX_4]^-$. The molecular structure of quadrivalent tellurium compounds has been discussed by T. M. Lowry and F. L. Gilbert [65] in the light of Drew's results.

The m. p. of chromium is probably 1920° or a little higher.[66] The electrodeposition of chromium from aqueous solutions of chromic acid has been studied by E. Müller and P. Ekwall [67] and by E. Liebreich and V. Duffek.[68] The number and nature of the hydrates formed by chromic sulphate have been examined,[69] and chromium ethoxide, $Cr(OEt)_3$, has been obtained by P. A. Thiessen and B. Kandelaky.[70] The kationic complexes containing six molecules of antipyrine or of urea for each $Cr^{\cdots}$ ion are readily formed and rather characteristic. Many salts of these complexes, as also of similar ones derived from other bi- and ter-valent metals, have been prepared.[71] Study of chromium oxide gels indicates that probably a definite compound Cr_2O_3,H_2O can exist, although the tendency for the gel to attain this state is very small.[72] A number of basic (Al, Zr, Sb, Bi, Fe) and normal (Cu, Cd, Co) chromates have been prepared by S. H. C. Briggs,[73] and the equilibrium $2CrO_4'' + 2H^{\cdot} \rightleftharpoons Cr_2O_7'' + H_2O$ has been studied by E. Carrière and P. Castel.[74]

A molybdoselenic acid and some ammonium molybdotellurates have been described.[75] H. M. Spittle and W. Wardlaw [76] have prepared a number of complex oxalate derivatives of quadrivalent molybdenum and, in particular, a series of the form

$$B_2[Mo_3O_4(C_2O_4)_3,5H_2O]$$
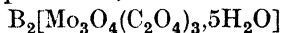
[65] *J.*, 1929, 2076; *A.*, 1218.

[66] C. J. Smithells and S. V. Williams, *Nature*, 1929, **124**, 617; *A.*, 1226.

[67] *Z. Elektrochem.*, 1929, **35**, 84; *A.*, 275.

[68] *Ber.*, 1929, **62**, [*B*], 2527; *A.*, 1402.

[69] F. Krauss, H. Querengässer, and P. Weyer, *Z. anorg. Chem.*, 1929, **179**, 413; *A.*, 663.

[70] *Ibid.*, **181**, 285; *A.*, 1027.

[71] E. Wilke-Dörfurt and H. G. Mureck, *ibid.*, **184**, 121; *A.*, 1930, 49; E. Wilke-Dörfurt and K. Niederer, *ibid.*, p. 145.

[72] A. Simon, O. Fischer, and T. Schmidt, *ibid.*, **185**, 107.

[73] *J.*, 1929, 242; *A.*, 411.

[74] *Compt. rend.*, 1928, **187**, 1292; *A.*, 140.

[75] E. Wendehorst, *Z. anorg. Chem.*, 1928, **176**, 233; *A.*, 40; V. W. Meloche and W. Woodstock, *J. Amer. Chem. Soc.*, 1929, **51**, 171; *A.*, 282.

[76] *J.*, 1929, 792; *A.*, 678.

(where $B = C_5H_5N$, K, or NH_4). Several salts derived from quinquevalent molybdenum have been described; they belong to three types, $R_2[MoOBr_5]$, $R[MoOBr_4]$, and $R[MoO_2Br_2,2H_2O]$.[77]

The binary systems composed of alkali (Li, Na, or K) molybdate with molybdenum trioxide and of the same alkali tungstate with tungsten trioxide have been examined, as well as the systems Li_2WO_4–Na_4WO_4 and Li_2MoO_4–K_2MoO_4.[78]

The growth of crystals of tungsten does not commence below 1200° if the powdered metal is heated in a stream of dry hydrogen. If the latter is moist, growth commences at 1050°, accompanied by loss in weight of the sample. These effects are due to the formation of WO_2, which is volatile at 1950°. The formation of large tungsten crystals in the reduction of the trioxide is due to the volatility of the oxides WO_3 and W_2O_5, which is measurable at 850° and 900° respectively.[79]

An abnormality that occurs in the temperature coefficient of the oxidation of tungsten in air between 850° and 950° is explained by supposing that tungsten oxide exists in two forms which are in equilibrium.[80] The reduction of tungsten trioxide by mixtures of carbon monoxide and dioxide takes place through the intermediate oxides W_2O_5 and WO_2. Between each oxide and the next, and between WO_2 and metal, there is a limited series of solid solutions. The constants for the successive stages of equilibrium have been determined, and the dissociation pressures of the three oxides of tungsten calculated.[81] The dissociation and volatilisation of MoS_2, WS_2, US_2, Al_2S_3, and MgS at very high temperatures in a vacuum have been examined by Picon.[82] A. G. Scroggie gives an improved method of preparing silicododecatungstic acid.[83] The gradual addition of hydrochloric acid to a solution of an alkali tungstate produces first a polymerisation to hexatungstic acid without any intermediate stage; the salts of this acid are identical with the paratungstates of the literature. With addition of more acid there is formed metatungstic acid, which is probably a diparatungstic acid, and in presence of other acids, such as arsenic or phosphoric acids, heteropolytungstic acids are formed. The changes $H_2WO_4 \longrightarrow H_6[W_6O_{21}] \longrightarrow H_8[As_2(W_2O_7)_9]$ are described in detail, and have been investigated by means of measurements

[77] F. G. Angell, R. G. James, and W. Wardlaw, *J.*, 1929, 2578; *A.*, 1930, 48.

[78] F. Hoermann, *Z. anorg. Chem.*, 1928, **177**, 145; *A.*, 160.

[79] G. A. Meierson, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1217; *A.*, 160.

[80] J. S. Dunn, *J.*, 1929, 1149; *A.*, 889.

[81] Z. Shibata, *Tech. Rep. Tôhoku Imp. Univ.*, 1929, **8**, 129, 145; *A.*, 651.

[82] *Bull. Soc. chim.*, 1929, [iv], **45**, 907; *A.*, 1930, 47.

[83] *J. Amer. Chem. Soc.*, 1929, **51**, 1057; *A.*, 779.

of diffusion coefficients and of absorption coefficients of visible and ultra-violet light.[84]

Metallic uranium of 99·95% purity has been prepared by heating U_3O_8 with sublimed calcium in an iron tube in a vacuum.[85]

An important paper has been published by L. Pauling [86] in which he formulates a set of principles governing the structure of complex ionic crystals. These are based on the assumption of a co-ordinated arrangement of anions about each kation at the corners of an approximately regular polyhedron. The known structures of many complex crystals satisfy these principles, by means of which it is shown that no stable basic silicates of bivalent metals can exist, and that in aluminium silicates of alkali metals there should be at least one aluminium ion for every alkali-metal ion. In a second paper,[87] the molecular structure of the tungstosilicates and related compounds is considered. The 12-hetero-poly-acids are given structures which may be represented by the formula

$$H_x[MO_4,W_{12}O_{18}(OH)_{36}]$$
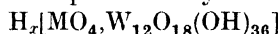
(where $x = 3, 4, 5, 6$ respectively when M = P, Si, B, H_2), in which 12 tungsten octahedra, slightly distorted and linked by 3 corners to each other, surround the undistorted MO_4 tetrahedron. Structures are also suggested for still more complex acids.

Group VII.

F. Fichter has continued his researches on the use of fluorine as an oxidising agent, with results which agree with his view that oxidation products so obtained are very similar to those obtained by anodic oxidation. During the past year the results obtained with salts of thallium, manganese, copper, and lead,[88] with nitric and perchloric acids,[89] and with alkaline acetate solutions [90] have been published. N. C. Jones also considers that, in the main, fluorine- and anodic-oxidation are similar, but criticises some of Fichter's views.[91] Anhydrous hydrogen fluoride with a specific electrical conductivity as low as 14×10^{-6} mho has been prepared by heating potassium hydrogen fluoride with rigorous precautions to exclude moisture.[92] According to P. Lebeau and A. Damiens,[93] a gas containing 70% of F_2O is formed by passing fluorine in fine

[84] G. Jander, D. Majert, and T. Aden, *Z. anorg. Chem.*, 1929, **180**, 129; *A.*, 664.

[85] E. Botolfsen, *Bull. Soc. chim.*, 1929, [iv], **45**, 626; *A.*, 1253.

[86] *J. Amer. Chem. Soc.*, 1929, **51**, 1010; *A.*, 748.

[87] *Idem, ibid.*, p. 2868; *A.*, 1367.

[88] F. Fichter and E. Brunner, *Helv. Chim. Acta*, 1929, **12**, 214; *A.*, 282.

[89] *Idem, ibid.*, p. 305; *A.*, 526.   [90] *Idem, ibid.*, p. 573; *A.*, 779.

[91] *J. Physical Chem.*, 1929, **33**, 801; *A.*, 891.

[92] K. Fredenhagen and G. Cadenbach, *Z. anorg. Chem.*, 1929, **178**, 289; *A.*, 411.

[93] *Compt. rend.*, 1929, **188**, 1253; *A.*, 779.

bubbles through a 2% solution of sodium hydroxide; it is collected over water, liquefied, and fractionated (b. p. $-167°$).

Chlorine fluoride, ClF, has been obtained as an almost colourless gas by the interaction of slightly moist chlorine and fluorine.[94] Spectrophotometric measurements indicate that, when carbon tetrachloride solutions of chlorine and bromine in equimolecular proportion are mixed, a compound BrCl is formed to the extent of about 50%.[95] H. J. Schumacher and G. Stieger [96] have described a method and apparatus for preparing chlorine hexoxide (Cl_2O_6 or ClO_3) in considerable quantities by the action of ozone on chlorine dioxide. It is a liquid with a vapour pressure of about 1 mm. at 20°, at which temperature, however, it slowly decomposes. A very unstable oxide of bromine (Br_3O_8)$_n$ is said to be formed by the action of ozone on bromine at $-5°$ to $10°$.[97] The solubilities of manganous fluoride have been measured, and a number of chemical observations recorded about it and cadmium fluoride.[98] The procedure required to obtain pure anhydrous hydrogen iodide has been described.[99] The solubility of iodine in solutions of halides has been measured at 25°; its value depends on two opposing factors : (a) the salting-out effect and (b) the tendency to form perhalides. With iodides, (a) is negligible, but with bromides and chlorides it is of considerable importance.[1] A chloroiodic acid, $HICl_4,4H_2O$, has been prepared by passing chlorine through a suspension of iodine in concentrated hydrochloric acid. At 0° it forms orange-yellow tabular crystals. Salts such as KCl,ICl_3 and $MgCl_2,2ICl_3,8H_2O$ are derived from this acid and possess an absorption band in common with it.[2] The phosphate, tri-, di-, and mono-chloroacetates, and the methanesulphonate of tervalent iodine have been prepared by Fouque's method.[3] A saturated solution of iodine acetate in acetic anhydride was electrolysed with a silvered platinum gauze cathode,

[94] O. Ruff, E. Ascher, J. Fischer, and F. Laass, *Z. anorg. Chem.*, 1928, **176,** 258; *A.*, 40; *idem* and F. Luft and H. Volkmer, *Z. angew. Chem.*, 1928, **41,** 1289; *A.*, 160; O. Ruff and F. Laass, *Z. anorg. Chem.*, 1929, **183,** 214; *A.*, 1226.

[95] S. Barratt and C. P. Stein, *Proc. Roy. Soc.*, 1929, [*A*], **122,** 582; *A.*, 411.

[96] *Z. anorg. Chem.*, 1929, **184,** 272; *A.*, 1930, 48.

[97] B. Lewis and H. J. Schumacher, *Z. physikal. Chem.*, 1928, **138,** 462; *A.*, 160; *Z. anorg. Chem.*, 1929, **182,** 182; *A.*, 1156; *Z. Elektrochem.*, 1929, **35,** 648; *A.*, 1395.

[98] P. Nuka, *Z. anorg. Chem.*, 1929, **180,** 235; *A.*, 779.

[99] R. T. Dillon and W. G. Young, *J. Amer. Chem. Soc.*, 1929, **51,** 2389; *A.*, 1156.

[1] J. S. Carter and C. R. Hoskins, *J.*, 1929, 580; *A.*, 501.

[2] V. Caglioti, *Atti R. Accad. Lincei*, 1929, [vi], **9,** 563; *A.*, 780.

[3] *Chem.-Ztg.*, 1914, **38,** 860.

and an amount of silver iodide was deposited equivalent to the current passed.[4] A quantitative study has been made of the oxidation of carbon monoxide by iodine pentoxide.[5] The electrolytic preparation of several permanganates, using anodes of silicomanganese and a platinum cathode separated by a diaphragm, has been described by G. Rapin.[6] Although neither manganese dioxide nor mercury will by itself dissolve in cold dilute sulphuric or nitric acid, they dissolve in presence of each other owing to the coupled reaction $MnO_2 + 2Hg + 4HNO_3 = Mn(NO_3)_2 + 2HgNO_3 + 2H_2O$ (or one giving Hg_2SO_4,Hg_2O) which is quantitative.[7] The preparation, properties, and nature of the oxides of manganese have been investigated.[8]

The crystal structure of rhenium resembles that of osmium. From the lattice constants and the atomic weight, the density of pure rhenium is calculated to be 21·4.[9] As much as a gram of pure rhenium has been prepared from Norwegian molybdenite having a rhenium content of $2-4 \times 10^{-6}$.[10]

White rhenium peroxide, Re_2O_8, is obtained by heating the metal or lower oxides in a stream of oxygen below 150°; near that temperature it melts and is converted into a yellow oxide, which is Re_2O_7, not ReO_3 as previously thought, and gives a strongly acid aqueous solution. The salts NH_4ReO_4, $NaReO_4$, and $Ba(ReO_4)_2$ have been prepared as white crystals and their solubilities determined. When the first two salts are heated in hydrogen to 400°, ReO_2 is formed as a black solid; from the solution of this dioxide in dilute nitric acid, barium rhenate, $BaReO_4$, was obtained.[11]

The crystal structure of potassium per-rhenate, $KReO_4$, has been examined.[12] It is isomorphous with scheelite.

Group VIII.

At 715° the solubility of oxygen in iron increases with increasing oxygen pressure to a maximum of 0·11%, above which value the formation of ferrous oxide begins.[13] The solubility of iron in car-

[4] F. Fichter and S. Stern, *Helv. Chim. Acta*, 1928, **11**, 1256; *A.*, 41.

[5] L. Rodriquez Pire, *Anal. Fís. Quím.*, 1929, **27**, 192; *A.*, 778.

[6] *Bull. Soc. chim.*, 1928, [iv], **43**, 1174; *A.*, 36; *Compt. rend.*, 1929, **188**, 1547; **189**, 287; *A.*, 891, 1151. See also J. Roudnick, *Bull. Soc. chim. Belg.*, 1929, **38**, 147; *A.*, 891.

[7] J. Meyer and R. Kanters, *Z. anorg. Chem.*, 1929, **185**, 172.

[8] *Idem, ibid.*, p. 177.

[9] V. M. Goldschmidt, *Naturwiss.*, 1929, **17**, 134; *A.*, 382; *Z. physikal. Chem.*, 1929, [*B*], **2**, 244; *A.*, 493.

[10] I. Noddack and W. Noddack, *Z. anorg. Chem.*, 1929, **183**, 353; *A.*, 1408.

[11] *Idem, Naturwiss.*, 1929, **17**, 93; *A.*, 411; *Z. anorg. Chem.*, 1929, **181**, 1; *A.*, 1027.

[12] E. Broch, *Z. physikal. Chem.*, 1929, [*B*], **6**, 22; *A.*, 1930, 20.

[13] W. Krings and J. Kempkens, *Z. anorg. Chem.*, 1929, **183**, 225; *A.*, 1230.

bonic acid solutions under carbon dioxide pressures of 20—50 atm. has been examined—it becomes almost independent of pressure above 30 atm.[14]

The presence of minute traces of iron in the salt is responsible for the red coloration which ammonium thiocyanate assumes when exposed to light. Ferric thiocyanate is formed by photochemical oxidation. This is reversed in the dark and the salt becomes colourless again.[15] Iron pentacarbonyl reacts with mercuric sulphate in 10% sulphuric acid to give $Fe(CO)_4Hg$, of which several reactions are described. By the action of halogens, compounds of the type $Fe(CO)_4X_2$ (X = Cl, Br, I) are obtained, and by the action of mercuric salts, compounds $Fe(CO)_4Hg,HgX_2$ are formed (X = Cl, Br, I, OAc, $\frac{1}{2}SO_4$).[16] When nitric oxide under pressure acts on iron carbonyl at 45°, a violent reaction occurs with formation of black crystals of unstable iron tetranitrosyl.[17] If the reaction is carried out in methyl-alcoholic solution, a black substance is formed which contains methyl alcohol and is probably $Fe(NO),2MeOH$.[18] The preparation of a number of further compounds of iron, cobalt, and nickel, containing nitric oxide, with the metal attached to sulphur and apparently univalent, has been described. The behaviour of these compounds has been compared with that of hyponitrites and shown to be different, and it is concluded that they really do contain univalent metal and have nitric oxide groupings attached to the metal by co-ordinated covalencies (donated by nitrogen).[19] The fluorides of the metals of Group VIII of the periodic system have been prepared and their physical and chemical properties tabulated.[20]

There are two hydrates of ferric fluoride, viz., $FeF_3,3H_2O$ and $FeF_3,4\cdot5H_2O$,[21] and ferrous bromide forms hydrates with 9, 6, 4, and 2 molecules of water. The solubility of ferrous bromide in water has been determined over the range − 60° to + 132°.[22] The reaction between ferric oxide and hydrogen sulphide has been examined between 120° and 830° : FeS_2 is the principal product

[14] E. Müller and H. Henecka, Z. anorg. Chem., 1929, **181**, 159; B., 751.

[15] C. G. Patten and H. D. Smith, Trans. Roy. Soc. Canada, 1928, (iii), **22**, III, 221; A., 407.

[16] H. Hock and H. Stuhlmann, Ber., 1929, **62**, [B], 431, 2690; A., 412; 1930, 47.

[17] W. Manchot and E. Enk, Annalen, 1929, **470**, 275; A., 1027.

[18] W. Manchot and H. Gall, ibid., p. 271; A., 1027.

[19] Idem, Ber., 1929, **62**, [B], 678; A., 526; W. Manchot and S. Davidson, ibid., p. 681; A., 526; W. Manchot and G. Lehmann, Annalen, 1929, **470**, 255; A., 1027; W. Manchot, ibid., p. 261; A., 1028.

[20] O. Ruff and E. Ascher, Z. anorg. Chem., 1929, **183**, 193; A., 1254.

[21] E. Deussen, Monatsh., 1929, **52**, 107; A., 1027.

[22] F. Schimmel, Ber., 1929, **62**, [B], 963; A., 665.

between 120° and 400°.[23]   Between 900° and 1000° magnetite, hæmatite, and iron pyrites will yield nearly all their iron as the volatile chloride on treatment with chlorine.[24]   The properties of the α- and γ-hydrates of ferric oxide have been examined; both are crystalline and, in a general way, correspond to the minerals goethite and lepidocrocite.[25]   Dark brown crystals of ferric ethoxide, $Fe(OEt)_3$, separate from a mixed solution of ferric chloride and sodium ethoxide in absolute alcohol.[26]   Cobalt forms only two oxides, CoO and Co_3O_4, but below about 100° the former can adsorb more oxygen to form CoO,nO_2 without any change in the crystal lattice.   At higher temperatures this changes into Co_3O_4,mO_2 with the lattice of Co_3O_4.   The dry methods for preparing cobaltic oxide found in the literature actually give Co_3O_4,mO_2.[27]   According to C. W. Stillwell,[28] the rose-coloured cobaltous hydroxide is the stable crystalline form; the blue varieties are unstable and the colour is structural.   One definite hydrate of cobaltic oxide, viz., Co_2O_3,H_2O, appears to exist.[29]   Cobaltous aluminate, chromite, ferrite, and cobaltite are true spinels,[30] but the nature of $CoO-ZnO$ mixtures depends on the proportion of the two oxides present.[31] A number of cobaltites, RO,Co_2O_3 ($R = Cu$, Mg, Zn, Mn, Ni) have been prepared and are of the spinel type.[32]   A new series of cobaltous compounds of the formula $R_2[CoX_4]$, where X is a halogen and R is pyridinium, quinolinium, or 2-methylquinolinium, has been prepared.[33]   The $CoCl_4''$ ion was postulated by Donnan and Bassett [34] to account for the blue colour of certain cobalt chloride solutions.

Crystals of $Co_2(SO_4)_3,18H_2O$ have been obtained by the action of ozone on a well-cooled solution of cobaltous sulphate in sulphuric acid.[35]   Lithium cobaltisulphite, $Li_3[Co(SO_3)_3],4H_2O$, has been prepared, and also the still less soluble potassium salt,

$$K_3[Co(SO_3)_3],6H_2O.^{36}$$
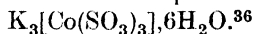
[23] L. A. Sayce, J., 1929, 2002; A., 1254.

[24] W. Kangro and R. Flügge, Z. Elektrochem., 1929, **35**, 189; A., 664.

[25] W. H. Albrecht, Ber., 1929, **62**, [B], 1475; A., 869; see also G. F. Hüttig and H. Garside, Z. anorg. Chem., 1929, **179**, 49; A., 510.

[26] P. A. Thiessen and O. Koerner, Z. anorg. Chem., 1929, **180**, 65; A., 675.

[27] M. Le Blanc and E. Möbius, Z. physikal. Chem., 1929, **142**, 151; A., 1028.

[28] J. Physical Chem., 1929, **33**, 1247; A., 1028.

[29] G. F. Hüttig and R. Kassler, Z. anorg. Chem., 1929, **184**, 279.

[30] G. Natta and L. Passorini, Gazzetta, 1929, **59**, 280; A., 870.

[31] Idem, ibid., p. 620; A., 1930, 20.

[32] S. Holgersson and A. Karlsson, Z. anorg. Chem., 1929, **183**, 384; A., 1409.

[33] E. G. V. Percival and W. Wardlaw, J., 1929, 1505; A., 1028.

[34] J., 1902, **81**, 939.

[35] E. Brunner, Helv. Chim. Acta, 1929, **12**, 208; A., 283.

[36] G. Jantsch and K. Abresch, Z. anorg. Chem., 1929, **179**, 345; A., 661.

The preparation of numerous amminated complex cobaltic compounds has been announced during the past year. Sometimes the structures suggested for individual compounds do not seem very probable, and in many cases, since no analytical support for the compounds is given, their very existence must be considered doubtful.[37] The manner in which oxalic and malonic acids act on tetramminocobaltic complexes and analogous compounds has been examined by W. Schramm,[38] whilst some of the factors determining the stability of complex salts have been discussed by F. G. Mann.[39] Experiments are quoted which suggest that, in the action of magnesium phenyl bromide on anhydrous nickel chloride, the very unstable nickel diphenyl is formed as an intermediate product, which is converted by hydrogen into nickel hydride, NiH_2, and benzene; in absence of hydrogen the products are nickel and diphenyl. Nickel hydride suspended in ether can hydrogenate ethylene slowly, and rapidly causes a mixture of ethylene and hydrogen to unite to form ethane.[40] Amine derivatives of cobalt and nickel nitrites have been prepared, and the dissociation pressure of hexamminonickel nitrite has been measured between 15° and 115°; the correspondence of the curve obtained with that found by Ephraim for the supposed pentammine shows the latter to be merely a mixture of hexammine and tetrammine.[41]

A study of ruthenium chloride solutions has shown that the first product of the action of concentrated hydrochloric acid on ruthenium tetroxide is RuO_2Cl_2, which is rapidly reduced further to ruthenium tetrachloride; this is unstable in solution, decomposing into either the trichloride or the hydroxytrichloride. From pure solutions of the latter can be prepared the " hydrated pentachlororuthenates," which are thus shown to be hydroxypentachlororuthenates.[42] The hydrates of rhodium sulphate have been examined and cæsium rhodium alum has been prepared.[43] A number of complex pyridine derivatives of rhodium trichloride [44] and pyridine and ammonia derivatives of iridium trichloride have been described, some of

[37] H. L. Riley, *J.*, 1928, 2985; *A.*, 41; S. H. C. Briggs, *J.*, 1929, 685; *A.*, 665; E. G. V. Percival and W. Wardlaw, *ibid.*, p. 1317; *A.*, 898; J. Kranig, *Ann. Chim.*, 1929, [x], **11**, 44; *A.*, 527; C. Duval, *Compt. rend.*, 1929, **188**, 176; *A.*, 283; C. Duval and (Mme.) Duval, *ibid.*, **189**, 537; *A.*, 1254; F. Job and L. O. Tao, *ibid.*, p. 641; *A.*, 1409.

[38] *Z. anorg. Chem.*, 1929, **180**, 161; *A.*, 780.

[39] *J.*, 1929, 651; *A.*, 678.

[40] T. Weichselfelder and M. Kossodo, *Ber.*, 1929, **62**, [*B*], 769; *A.*, 665.

[41] L. Le Boucher, *Anal. Fis. Quim.*, 1929, **27**, 145, 358; *A.*, 781, 898.

[42] H. Remy and A. Lührs, *Ber.*, 1929, **62**, [*B*], 200; *A.*, 283.

[43] F. Krauss and H. Umbach, *Z. anorg. Chem.*, 1929, **180**, 42; **182**, 411; *A.*, 665, 1156.

[44] M. Delépine, *Bull. Soc. chim.*, 1929, [iv], **45**, 235; *A.*, 781.

which exist in *cis-* and *trans-*forms.[45]   The complex ion, $[Rh(CN)_6]'''$, is said to be very stable, contrary to previous reports in the literature.[46]   The sole product of the action of fluorine on powdered iridium at 260° is the hexafluoride,[47] a very volatile, highly reactive, yellow substance, m. p. 44°.   Iridium tetrafluoride may be prepared by heating powdered iridium with the hexafluoride at 150°.   Lithium platinocyanide forms only one hydrate—the tetrahydrate—which is said to exist in three differently coloured forms.[48]   A number of complex platinum compounds have been obtained by the oxidation with ammonium persulphate of Peyrone's salt and the green Magnus salt.[49]

Systems and Equilibria.

Owing to the importance of phase-rule investigations for inorganic chemistry a list of systems which have been examined during the last year is here given, in the order in which they appear in the abstracts, as was done in last year's Annual Report.

Zinc oxide–water [50]; calcium oxide–aluminium oxide; calcium oxide–zirconium oxide; aluminium oxide–zirconium oxide [51]; lithium chloride–ammonia [52]; cupric bromide–hydrobromic acid–water [53]; ammonium sulphate–sulphuric acid–ethyl alcohol [54]; ferrous chloride–water [55]; sodium oxalate–sulphuric acid–sodium sulphate (or oxalic acid)–water [56]; iron–zinc [57]; tungsten–carbon [58]; ammonium sulphite–water [59]; aluminium–copper–zinc [60]; lead nitrate–ammonium nitrate–water [61]; aluminium nitrate–potassium

[45] M. Delépine and J. Pineau, *Bull. Soc. chim.*, 1929, [iv], **45,** p. 228; *A.*, 781.
[46] F. Krauss and H. Umbach, *Z. anorg. Chem.*, 1929, **179,** 357; *A.*, 665.
[47] O. Ruff and J. Fischer, *ibid.*, p. 161; *A.*, 527.
[48] F. E. E. Germann and O. B. Muench, *J. Physical Chem.*, 1929, **33,** 415; *A.*, 527.
[49] L. Tschugaev and J. Tscherniaev, *Z. anorg. Chem.*, 1929, **182,** 159; *A.*, 1157.
[50] A. Gutbier and H. R. Barfuss-Knochendöppel, *ibid.*, 1928, **176,** 363; *A.*, 30.
[51] H. von Wartenberg, H. Linde, and R. Jung, *ibid.*, p. 349; *A.*, 30.
[52] S. C. Collins and F. K. Cameron, *J. Physical Chem.*, 1928, **32,** 1705; *A.*, 30.
[53] S. R. Carter and N. J. L. Megson, *J.*, 1928, 2954; *A.*, 30.
[54] H. B. Dunnicliff, A. L. Aggarwal, and R. C. Hoon, *J. Physical Chem.*, 1928, **32,** 1697; *A.*, 31.
[55] F. Schimmel, *Z. anorg. Chem.*, 1928, **176,** 285; *A.*, 31.
[56] E. Elöd and E. Acker, *ibid.*, p. 305; *A.*, 32.
[57] Y. Ogawa and T. Murakami, *Tech. Rep. Tôhoku*, 1928, **8,** 53; *A.*, 141.
[58] K. Becker, *Z. Metallk.*, 1928, **20,** 437; *A.*, 141.
[59] F. Ishikawa and H. Murooka, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1928, **7,** 1160; *A.*, 141.
[60] M. Hamasumi and S. Matoba, *Tech. Rep. Tôhoku*, 1928, **8,** 71; *A.*, 141.
[61] G. Malquori, *Atti II Cong. Naz. Chim. pura appl.*, 1926, 1135; *Chem. Zentr.*, 1928, ii, 517; *A.*, 141.

nitrate–nitric acid–water [62]; potassium chloride–ferric chloride–water; aluminium chloride–ferric chloride–water [63]; sodium nitrate–magnesium sulphate–water [64]; nitrates and sulphates of sodium (and potassium)–water [65]; thallous chloride–water–chloride of Cd (or Hg", Zn, Mg, Ca, Sr, Ba) [66]; manganese chloride–cobalt chloride; cadmium chloride–cobalt chloride; magnesium chloride–cobalt chloride [67]; magnesium–zinc [68]; cadmium–gold [69]; silver–copper [70]; cobalt–sulphur–oxygen; nickel–sulphur–oxygen [71]; calcium–sulphur–oxygen [72]; iron–carbon–oxygen [73]; ammonium sulphite–ammonium sulphate–water [74]; sodium nitrate–sodium chloride–water [75]; mercuric iodide–potassium iodide–acetone [76]; cadmium–lead chloride [77]; lead acetate–lead chloride–acetic acid–water [78]; sodium nitrate–sodium sulphate–magnesium chloride–water [79]; magnesium chloride–ferrous chloride; cadmium chloride–ferrous chloride [80]; cæsium sulphate–cerous sulphate–water [81]; mercuric chloride–mercuric iodide–water [82]; sodium nitrate–potassium nitrate–water [83]; sodium–calcium [84]; calcium oxide–zirconium

[62] G. Malquori, *Gazzetta*, 1928, **58**, 781; *A.*, 142.

[63] *Idem, ibid.*, p. 891; *A.*, 267.

[64] W. Schröder, *Z. anorg. Chem.*, 1928, **177**, 71; 1929, **184**, 63, 77; **185**, 153; *A.*, 267; *Caliche*, 1929, **11**, 154.

[65] E. Cornec and H. Krombach, *ibid.*, 1928, **10**, 396; *A.*, 267.

[66] A. Benrath and G. Ammer, *Z. anorg. Chem.*, 1928, **177**, 129; *A.*, 267.

[67] A. Ferrari and A. Inganni, *Atti R. Accad. Lincei*, 1928, [vi], **8**, 238; *A.*, 388.

[68] W. Hume-Rothery and E. O. Rounsefell, *Inst. Metals*, March 1929, Advance copy; *A.*, 398.

[69] P. J. Durrant, *ibid.*; *A.*, 398.

[70] J. A. A. Leroux and E. Raub, *Z. anorg. Chem.*, 1929, **178**, 257; *A.*, 399.

[71] R. Schenck and E. Raub, *ibid.*, p. 225; *A.*, 399.

[72] R. Schenck and K. Jordan, *ibid.*, p. 389; *A.*, 399.

[73] E. Jänecke, *ibid.*, p. 73; *A.*, 399.

[74] F. Ishikawa and H. Murooka, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1929, **8**, 75; *A.*, 400.

[75] A. Chrétien and E. Cornec, *Compt. rend.*, 1929, **188**, 628; *A.*, 400.

[76] (Mlle.) M. Pernot, *ibid.*, p. 635; **189**, 326; *A.*, 400, 1145.

[77] R. Lorenz and M. Hering, *Z. anorg. Chem.*, 1928, **177**, 1; *A.*, 266; *ibid.*, 1929, **178**, 33, 40, 337; *A.*, 400; R. Lorenz, G. Schulz, M. Hering, P. Wolff, and J. Silberstein, *ibid.*, **179**, 97; *A.*, 510.

[78] K. Sandved, *J.*, 1929, 337; *A.*, 400.

[79] G. Leimbach and A. Pfeiffenberger, *Caliche*, 1929, **10**, 447; **11**, 61; *A.*, 400, 1013.

[80] A. Ferrari and M. Carugati, *Atti R. Accad. Lincei*, 1928, [vi], **8**, 306; *A.*, 500.

[81] F. Zambonini and S. Restaino, *ibid.*, 1929, **9**, 131; *A.*, 510.

[82] (Miss) R. Sugden, *J.*, 1929, 488; *A.*, 510.

[83] E. Cornec and H. Krombach, *Compt. rend.*, 1929, **188**, 788; *A.*, 510.

[84] R. Lorenz and R. Winzer, *Z. anorg. Chem.*, 1929, **179**, 281; *A.*, 650.

oxide [85]; sodium sulphate–water–sulphate of Cu (or Mg, Zn, Cd, Mn, Fe'', Co, Ni) [86]; sodium nitrate–potassium perchlorate–water [87]; sodium chloride–potassium perchlorate–water [88]; sodium nitrate–sodium chloride–potassium perchlorate–water.[89]

CaO–CdO; CaO–MnO; CaO–CoO; CaO–NiO; CaO–MgO; CoO–NiO; CoO–MgO; CoO–MnO; CoO–CdO; NiO–MgO; NiO–MnO; NiO–CdO [90]; sodium nitrate–sodium sulphate–water [91]; ferric nitrate–nitric acid–water [92]; potassium nitrate–ferric nitrate–nitric acid–water [93]; strontium oxide–phosphoric oxide–water; barium oxide–phosphoric oxide–water [94]; thallous sulphate–mercuric chloride, bromide, or iodide [95]; thallous nitrate–potassium bromide [96]; cadmium–antimony [97]; chromium–nitrogen; manganese–nitrogen [98]; zirconium oxide–thorium oxide [99]; ammonium nitrate–carbamide [1]; cupric sulphate–ferrous sulphate–water [2]; sodium iodate–sodium chloride–water [3]; sodium and potassium nitrates and sulphates–water [4]; aluminium nitrate–ferric nitrate–water; potassium nitrate–ferric nitrate–water [5]; lanthanum nitrate–manganese nitrate–water; lanthanum nitrate–magnesium nitrate–water; manganese nitrate–magnesium nitrate–water [6]; ammonium hydrogen carbonate–water [7]; aluminium–

[85] O. Ruff, F. Ebert, and E. Stephan, Z. anorg. Chem., 1929, 180, 215; A., 650; O. Ruff, Z. angew. Chem., 1929, 42, 807; A., 1161.

[86] A. Benrath and H. Benrath, Z. anorg. Chem., 1929, 179, 369; 183, 296; A., 650, 1238.

[87] E. Cornec and A. Neumeister, Caliche, 1929, 11, 488; A., 650.

[88] Idem, ibid., p. 492; A., 650.

[89] Idem, ibid., p. 494; A., 650.

[90] G. Natta and L. Passerini, Gazzetta, 1929, 59, 129, 144; A., 639.

[91] A. Chrétien, Compt. rend., 1929, 188, 1047; A., 651.

[92] G. Malquori, Atti R. Accad. Lincei, 1929, [vi], 9, 324; A., 651.

[93] Idem, ibid., p. 414; A., 651.

[94] H. V. Tartar and J. R. Lorah, J. Amer. Chem. Soc., 1929, 51, 1091; A., 651.

[95] N. K. Voskressenskaja, J. Russ. Phys. Chem. Soc., 1929, 61, 79; A., 651.

[96] A. P. Rostkovski, ibid., p. 89; A., 651.

[97] T. Murakami and T. Shinagawa, J. Study Met., 1928, 5, 283; A., 766.

[98] G. Valensi, J. Chim. physique, 1929, 26, 152, 202; A., 664, 766.

[99] O. Ruff, F. Ebert, and H. Woitinek, Z. anorg. Chem., 1929, 180, 252; A., 766; O. Ruff, Z. angew. Chem., 1929, 42, 807; A., 1161.

[1] W. J. Howells, J., 1929, 910; A., 766.

[2] F. K. Cameron and H. D. Crockford, J. Physical Chem., 1929, 33, 709; A., 767.

[3] H. W. Foote and J. E. Vance, Amer. J. Sci., 1929, [v], 17, 424; A., 767.

[4] E. Cornec, H. Krombach, and A. Spack, Compt. rend., 1929, 188, 1250; A., 767.

[5] G. Malquori, Atti R. Accad. Lincei, 1929, [vi], 9, 569; A., 767.

[6] C. di Capua, Gazzetta, 1929, 59, 164; A., 767.

[7] E. Jänecke, Z. Elektrochem., 1929, 35, 332; A., 874.

copper–nickel [8]; iron–molybdenum [9]; cupric oxide–sulphur trioxide–water [10]; calcium oxide–carbon dioxide–silica [11]; aluminium–antimony–silicon; aluminium–antimony–copper [12]; sodium and potassium carbonates and hydrogen carbonates–water [13]; zinc sulphide–zinc 'sulphate–zinc oxide–sulphur dioxide [14]; copper–aluminium–tin (or cobalt) [15]; copper–beryllium [16]; silver–germanium [17]; cobalt chloride–ferrous chloride; manganous chloride–ferrous chloride [18]; $Na_2O-N_2O_5-HCl-H_2O$; $K_2O-N_2O_5-HCl-H_2O$; $Na_2O-K_2O-N_2O_5-H_2O$; $Na_2O-K_2O-HCl-H_2O$ [19]; gold–mercury [20]; iron–vanadium [21]; calcium and sodium and their chlorides [22]; silver chloride–potassium iodide [23]; sodium oxide–boric oxide–sodium chloride; sodium oxide–boric oxide–sodium bromide [24]; lithium chlorate–water [25]; lead chloride–lead fluoride (or litharge or lead iodide, or silver chloride, or cuprous chloride); mercuric iodide–cadmium iodide (or mercurous iodide) [26]; sodium hydrogen carbonate–potassium hydrogen carbonate–water [27]; potassium carbonate–potassium sulphate–water [28]; uranyl formate–formic acid–water [29]; sodium thiocyanate–water (or methyl or ethyl

[8] H. Nishimura, *Suiyokaishi*, 1928, **5**, 616; *A.*, 883.

[9] T. Takei and T. Murakami, *Sci. Rep. Tôhoku Imp. Univ.*, 1929, **18**, 135; *A.*, 884.

[10] E. Posnjak and G. Tunell, *Amer. J. Sci.*, 1929, [v], **18**, 1; *A.*, 884.

[11] G. F. Hüttig and E. Rosenkranz, *Z. Elektrochem.*, 1929, **35**, 308; *A.*, 884.

[12] T. Matsukawa, *Suiyokaishi*, 1928, **5**, 596; *A.*, 884.

[13] A. E. Hill and S. B. Smith, *J. Amer. Chem. Soc.*, 1929, **51**, 1626; *A.*, 884.

[14] M. Trautz and S. Pakschwer, *J. pr. Chem.*, 1929, [ii], **122**, 147; *A.*, 884.

[15] E. Morlet, *Compt. rend.*, 1929, **189**, 102; *A.*, 995.

[16] G. Masing and O. Dahl, *Wiss. Veröff. Siemens-Konz.*, 1929, **8**, (1), 94; *A.*, 995.

[17] T. R. Briggs, R. O. McDuffie, and L. H. Willisford, *J. Physical Chem.*, 1929, **33**, 1080; *A.*, 996.

[18] A. Ferrari, A. Celeri, and F. Giorgi, *Atti R. Accad. Lincei*, 1929, [vi], **9**, 782; *A.*, 996.

[19] V. I. Nikolaev, *Z. anorg. Chem.*, 1929, **181**, 249; *A.*, 1010.

[20] A. A. Sunier and B. E. Gramkee, *J. Amer. Chem. Soc.*, 1929, **51**, 1703; *A.*, 874; I. Plaksin, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 521; *A.*, 1012.

[21] S. Oya, *J. Study Met.*, 1928, **5**, 349; *A.*, 1012.

[22] R. Lorenz and R. Winzer, *Z. anorg. Chem.*, 1929, **181**, 193; **183**, 127; *A.*, 1012, 1238.

[23] A. P. Rostkowski, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 595; *A.*, 1012.

[24] B. Stålhane, *Z. Elektrochem.*, 1929, **35**, 486; *A.*, 1012.

[25] L. Berg, *Z. anorg. Chem.*, 1929, **181**, 131; *A.*, 1145.

[26] H. Pélabon and (Mme.) Lande, *Bull. Soc. chim.*, 1929, [iv], **45**, 488; *A.*, 1145.

[27] N. E. Oglesby, *J. Amer. Chem. Soc.*, 1929, **51**, 2352; *A.*, 1145.

[28] A. E. Hill and S. Moskowitz, *ibid.*, p. 2396; *A.*, 1145.

[29] A. Colani, *Bull. Soc. chim.*, 1929, [iv], **45**, 624; *A.*, 1238.

alcohol, or acetone) [30]; sodium ferrocyanide–water [31]; lithium sulphate–water [32]; lithium thiocyanate–water [33]; leucite–diopside [34]; nitrates and chlorides of sodium and potassium–water [35]; sodium nitrate–sodium chloride–sodium sulphate–water [36]; aluminium chloride–ferric chloride–potassium chloride–hydrogen chloride–water [37]; sodium sulphide–ferrous sulphide [38]; potassium metasilicate–silica [39]; chromium–carbon [40]; sodium and potassium nitrates, chlorides, and sulphates–water [41]; copper–zinc [42]; potassium nitrate–magnesium sulphate–water [43]; silver–zinc [44]; magnesium sulphate–sodium nitrate–water [45]; sodium iodate–sodium nitrate–water [46]; strontium oxide–sucrose–water.[47]

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[32] J. A. N. Friend, *ibid.*, p. 2330; *A.*, 1375.

[33] V. I. Nikolaev, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 939; *A.*, 1387.

[34] N. L. Bowen and J. F. Schairer, *Amer. J. Sci.*, 1929, [v], **18**, 301; *A.*, 1388.

[35] E. Cornec and H. Krombach, *Caliche*, 1928, **10**, 153; *Chem. Zentr.*, 1929, i, 2740; *A.*, 1388.

[36] A. Chrétien, *Ann. Chim.*, 1929, [x], **12**, 9; *A.*, 1388.

[37] G. Malquori, *Gazzetta*, 1929, **59**, 556; *A.*, 1388.

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[39] F. C. Kracek, N. L. Bowen, and G. W. Morey, *J. Physical Chem.*, 1929, **33**, 1857.

[40] R. Kraiczek and F. Sauerwald, *Z. anorg. Chem.*, 1929, **185**, 193.

[41] E. Cornec and H. Krombach, *Ann. Chim.*, 1929, **12**, 203; *Caliche*, 1928, **10**, 250; *Chem. Zentr.*, 1929, i, 2741; *A.*, 1388.

[42] R. Ruer and K. Kremers, *Z. anorg. Chem.*, 1929, **184**, 193.

[43] A. and H. Benrath, *ibid.*, p. 359.

[44] B. G. Petrenko, *ibid.*, p. 369; G. J. Petrenko, *ibid.*, p. 376; G. J. and B. G. Petrenko, *ibid.*, **185**, 96.

[45] A. Benrath and co-workers, *Caliche*, 1929, **11**, 99; *A.*, 1930, 36.

[46] H. W. Foote and J. E. Vance, *Amer. J. Sci.*, 1929, [v], **18**, 375; *A.*, 1930, 36.

[47] W. Reinders and A. Klinkenburg, *Rec. trav. chim.*, 1929, **48**, 1227; *A.*, 1930, 36.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

Space Formulæ of Simple Carbon Compounds.

SOME early work [1] on the crystalline structure of pentaerythritol seemed to point to a pyramidal grouping of the four $CH_2 \cdot OH$ groups round the central carbon atom, in place of the usually accepted tetrahedral distribution. Although this conclusion was not supported by the whole of the crystallographic data,[2] there appeared to be sufficient evidence, both in this case and in that of methane, to raise a question of fundamental importance in stereochemical [3] theory.

On the chemical side the constitution of the substance as $C(CH_2 \cdot OH)_4$ has been confirmed by its transformation into $\beta\beta$-dimethylpropane-$\alpha\gamma$-diol,[4] the structure of which is known. An attempt has been made by J. Böeseken and B. B. C. Felix [5] to decide between the tetrahedral and the pyramidal configuration by forming compounds of the type $C(<^{CH_2 \cdot O}_{CH_2 \cdot O}>CRR')_2$, which are obtained by the condensation of pentaerythritol with 2 molecules of an aldehyde, ketone, or ketonic acid. If the configuration is tetrahedral, the condensation compound must be dissymmetric and capable of resolution; but if pyramidal, cis–trans isomerism will be encountered. Experiment showed that it was possible to resolve the acid $C(<^{CH_2 \cdot O}_{CH_2 \cdot O}>CMe \cdot CO_2H)_2$ obtained by condensation of pentaerythritol with ethyl pyruvate and hydrolysis of the resulting ester. This resolution, as is pointed out by A. Semenzov,[6] does not by itself establish the tetrahedral structure of pentaerythritol, since on examination the pyramidal model of the trans-form of the condensation product is seen to be dissymmetric. It has been suggested also that chemical methods are not suitable for testing the validity of Weissenberg's principle, owing to the possibility of transformation

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[1] H. Mark and K. Weissenberg, Z. Physik, 1923, **17**, 301; A., 1923, i, 1055.

[2] See Ann. Reports, 1927, **24**, 290.

[3] K. Weissenberg, Ber., 1926, **59**, [B], 1526; A., 1926, 934.

[4] H. Bincer and K. Hess, Ber., 1928, **61**, [B], 537; A., 1928, 504.

[5] Ibid., pp. 787, 1855; 1929, **62**, [B], 1310; A., 1928, 616, 1213; 1929, 791.

[6] Ibid., 1929, **62**, [B], 514; A., 538.

to a tetrahedral configuration during the reaction.[7] In reply, Böeseken and Felix maintain that enantiomorphs of the pyramidal type would be so labile as to render their isolation most improbable. The accomplished resolution of the sole reaction product, together with the failure to detect any trace of *cis–trans* isomerides, may therefore be taken as evidence in favour of the tetrahedral configuration. A recent crystallographic examination of the tetra-acetate of pentaerythritol by the X-ray method tends to confirm this view.[8]

Crystal analysis of solid methane has failed to provide evidence of the occurrence of pyramidal molecules and here also tetrahedral symmetry is encountered.[9] There is some evidence that two of the C·H linkings in methane differ slightly from the other two,[10] but the inequality, although perhaps sufficient to account for the electric moment and the infra-red absorption spectrum of methane, is presumably not great enough to be recognised as a non-equivalence of valency from the chemical point of view.

If the carbon valencies show perfect tetrahedral symmetry, the angle between each pair will be 109° 28′, and in certain long-chain aliphatic compounds this value appears to be very nearly preserved in the angles formed by the lines joining the centres of successive carbon atoms.[11] On the other hand, the results of an X-ray examination of a series of fatty acid salts demand a minimum angle of 111° 46′, and it is possible that even in these comparatively simple cases, in which the carbon chain appears to be zig-zag in shape, the angle throughout the chain may be dependent on the nature of the end groups.[12] It is probable, therefore, that in almost all carbon compounds a departure from the exact value of the tetrahedral angle is to be expected.[13]

Partly Substituted Glycerols.

Comment was made in an earlier Report [14] on the uncertainty attaching to the structure of the alleged β-monoacyl derivatives of glycerol. Many additional examples of the wandering of substituent acyl groups within the glycerol molecule have come to light recently and, although methods are now available for the synthesis of true

[7] J. Kenner, *Ber.*, 1928, **61**, [*B*], 2470; *A.*, 171.

[8] (Miss) I. E. Knaggs, *Proc. Roy. Soc.*, 1929, [*A*], **122**, 69; *A.*, 246.

[9] J. C. McLennan and W. G. Plummer, *Phil. Mag.*, 1929, [vii], **7**, 761; *A.*, 750.

[10] G. W. Brindley, *Nature*, 1929, **123**, 760; *A.*, 629.

[11] A. Müller, *Proc. Roy. Soc.*, 1929, [*A*], **124**, 317; *A.*, 869.

[12] S. H. Piper, *J.*, 1929, 234; *A.*, 383.

[13] Compare B. V. Nekrassov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 19; *A.*, 1928, 613.

[14] *Ann. Reports*, 1927, **24**, 90.

β-acyl derivatives,[15] the situation regarding the disubstituted derivatives is still confused, several supposed αβ-derivatives having been found to be identical with their αγ-isomerides.[16] For example, it has been proved that the supposed αβ- and αγ-diphthalimido-derivatives of glycerol, prepared according to the schemes outlined below, are identical, as are also the monoacetates and monobenzoates

$$
\begin{array}{ccccc}
\text{CH}_2 & \text{CH}_2\text{Cl} & \text{CH}_2\text{X} & \text{CH}_2\text{X} & \text{CH}_2\text{Cl} \\
\text{CH} \longrightarrow & \text{CHCl} \longrightarrow & \text{CHX} & \text{CH·OH} \longleftarrow & \text{CH·OH} \\
\text{CH}_2\text{·OH} & \text{CH}_2\text{·OH} & \text{CH}_2\text{·OH} & \text{CH}_2\text{X} & \text{CH}_2\text{Cl}
\end{array}
$$

$$(X = \cdot N{<}^{CO}_{CO}{>}C_6H_4)$$

Identical
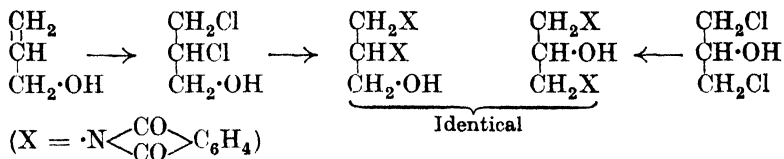
of the αβ- and αγ-diphthalimido-derivatives, which have been prepared by independent methods. On the other hand, different dibromohydrin p-nitrobenzoates have been obtained, and a similar series of reactions served to produce different dibromohydrin

$$
\begin{array}{ccccc}
\text{CH}_2 & \text{CH}_2\text{Br} & \text{CH}_2\text{Br} & \text{CH}_2\text{Br} & \text{CH}_2\text{Br} \\
\text{CH} \longrightarrow & \text{CHBr} \longrightarrow & \text{CHBr} & \text{CH·OY} \longleftarrow & \text{CH·OH} \\
\text{CH}_2\text{·OH} & \text{CH}_2\text{·OH} & \text{CH}_2\text{·OY} & \text{CH}_2\text{Br} & \text{CH}_2\text{Br}
\end{array}
$$

$$(Y = \cdot CO\cdot C_6H_4\cdot NO_2)$$
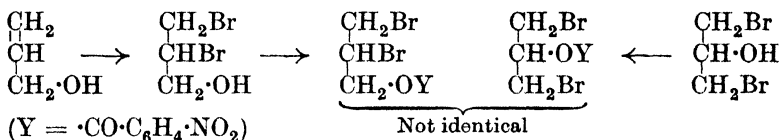
Not identical

palmitates. The latter substances reacted, however, to give identical di-p-nitrobenzoates. In many of these transformations migration of an acyl group must have occurred, rendering the allocation of structural formulæ difficult and uncertain. The conclusion was reached by Fairbourne and Cowdrey that the only absolute proof of unsymmetrical structure, in disubstituted derivatives of glycerol, is furnished by resolution into optically active forms,[17] and these authors suggest that in the absence of such evidence it is reasonable to assume that, when a disubstituted glycerol exists as two isomerides, these have the structures of their respective parent substances, but that in all other cases conversion may have occurred.

The cyclic acetals derived from glycerol furnish even greater possibilities for complex behaviour. It was thought at one time that when an aldehyde, R·CHO, condenses with glycerol, only the αβ-hydroxyl groups of the latter react, giving a cyclic acetal with a five-membered ring.[18] Recent work has shown, however, that in

[15] B. Helferich and H. Sieber, Z. physiol. Chem., 1928, 175, 311; A., 1928, 734.

[16] A. Fairbourne and G. W. Cowdrey, J., 1929, 129; A., 292; compare H. Hibbert and N. M. Carter, J. Amer. Chem. Soc., 1929, 51, 1601; A., 791.

[17] Compare M. Bergmann, Z. physiol. Chem., 1924, 137, 47; A., 1924, i, 932.

[18] J. C. Irvine, J. L. A. Macdonald, and C. W. Soutar, J., 1915, 107, 337.

reality there is a partition of the aldehyde between the αβ- and the αγ-hydroxyl groups with the formation of both five-membered and six-membered rings. In such cases there is not only the possibility of transformation from one ring form to the other, but also the added complication that the cyclic acetals of glycerol may possess geometrical and optical, in addition to structural, isomerism.[19] It is obvious, for instance, that (A) can give two geometric isomerides which are resolvable racemic forms owing to the presence of the

(A)

$$H\!\!\diagdown\!\!\underset{HO \cdot H_2C\diagup}{\overset{*}{C}}\!\!\diagup\!\!\overset{CH_2-O}{\underset{O}{\diagdown}}\!\!\diagdown\!\!\overset{*}{C}\!\!\diagup\!\!\overset{H}{\diagdown}R$$

$$H\!\!\diagdown\!\!\underset{HO\diagup}{C}\!\!\diagup\!\!\overset{CH_2-O}{\underset{CH_2-O}{\diagdown}}\!\!\diagdown\!\!C\!\!\diagup\!\!\overset{H}{\diagdown}R$$

(B)
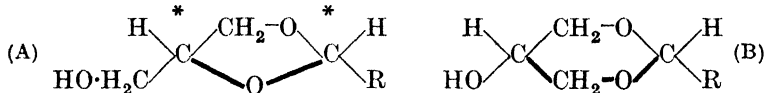
two centres of dissymmetry (*), and that (B) should exist in two geometrically isomeric but non-resolvable modifications.

In view of this intricacy it is particularly satisfactory to find that in certain cases a complete solution of the problems presented by the structural and geometric isomerism of these acetals has been achieved. If formaldehyde is condensed with glycerol, geometric isomerism corresponding to formulæ (A) and (B) becomes impossible (R = H) and two structurally isomeric methylene glycerols should exist, one of which ought to be resolvable. In accordance with theory a mixture of the αβ- and αγ-methylene glycerols was obtained when trioxymethylene was condensed with glycerol.[20] The isomerides were separated as the benzoyl derivatives and the structures of the latter compounds were proved by removal of the benzoyl group, followed by methylation to the corresponding monomethyl ethers, the subsequent hydrolysis of which gave respectively the α- and the β-methyl ether of glycerol. The reactions involved in the case of the αγ-compound are summarised in the following formulæ. A similar series holds for the racemic αβ-compound, the partial resolution of which was effected by D. H. Peacock [21] several years ago.

$$\begin{array}{c} CH_2 \cdot O \\ CH \cdot OH \\ CH_2 \cdot O \end{array}\!\!\!\diagdown CH_2 \longrightarrow \begin{array}{c} CH_2 \cdot O \\ CH \cdot OBz \\ CH_2 \cdot O \end{array}\!\!\!\diagdown CH_2 \longrightarrow \begin{array}{c} CH_2 \cdot O \\ CH \cdot OH \\ CH_2 \cdot O \end{array}\!\!\!\diagdown CH_2 \longrightarrow$$

Mixed with αβ-compound

$$\begin{array}{c} CH_2 \cdot O \\ CH \cdot OMe \\ CH_2 \cdot O \end{array}\!\!\!\diagdown CH_2 \longrightarrow \begin{array}{c} CH_2 \cdot OH \\ CH \cdot OMe \\ CH_2 \cdot OH \end{array}$$
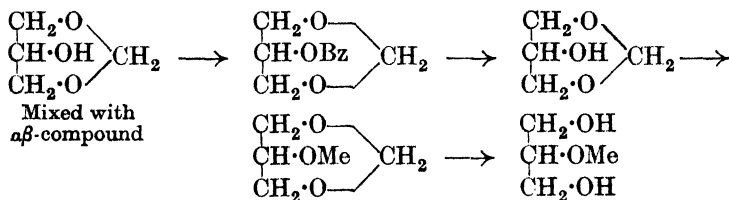
It is to be noted that in the presence of a trace of acid the αβ-acetal readily isomerises into the αγ-derivative, the six-membered ring

[19] H. Hibbert and N. M. Carter, *J. Amer. Chem. Soc.*, 1928, **50**, 3120; *A.*, 47.

[20] *Idem, ibid.*   [21] *J.*, 1915, **107**, 815; *A.*, 1915, i, 767.

being therefore the more stable under these conditions.   In alkaline media no evidence of a tendency to isomerise was obtainable.

Condensation of glycerol with p-nitrobenzaldehyde [22] gives p-nitrobenzylidene derivatives corresponding to formulæ (A) and (B) above (R $= C_6H_4\cdot NO_2$).   In this case structurally different isomerides were readily isolated and certain derivatives of these, namely, the benzoates, the p-nitrobenzoates, and the methyl ethers, were found to show the maximum number of isomerides theoretically possible, $i.e.$, two racemic geometric isomerides containing a five-membered ring, and two geometric isomerides containing a six-membered ring.   The proof of ring structure was again obtained by the methylation method and depended on the identification of the glycerol monomethyl ether left after removal of the p-nitrobenzylidene group.   Both the $\alpha\beta$- and the $\alpha\gamma$-p-nitrobenzylidene glycerol underwent rapid isomerisation in the presence of 0·01% of hydrogen chloride, giving in each case an equilibrium mixture which contained the two forms in the proportion of five parts of the $\alpha\beta$- to one part of the $\alpha\gamma$-compound.

The utilisation of the methyl ethers of glycerol as reference substances for the determination of configuration in the glycerol series may now be expected to give important information concerning the structure of the disubstituted glycerols.   Hitherto the methylation method was unavailable in such cases owing to the supposed impossibility of obtaining the β-monomethyl ether.   An attempt to prepare this substance was made by H. S. Gilchrist and C. B. Purves,[23] who utilised the following series of reactions :

$$\begin{array}{ccccc} \text{CH}_2\text{Cl} & \text{CH}_2\text{Cl} & \text{CH}_2\cdot\text{OAc} & \text{CH}_2\cdot\text{OH} \\ \text{CH}\cdot\text{OH} \longrightarrow & \text{CH}\cdot\text{OMe} \longrightarrow & \text{CH}\cdot\text{OMe} \longrightarrow & \text{CH}\cdot\text{OMe} \\ \text{CH}_2\text{Cl} & \text{CH}_2\text{Cl} & \text{CH}_2\cdot\text{OAc} & \text{CH}_2\cdot\text{OH} \end{array}$$
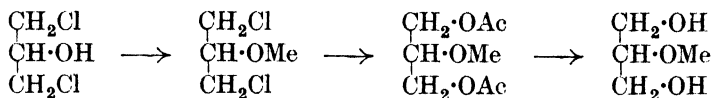
They identified their product (erroneously) as glycerol α-methyl ether, alleging that the $\alpha\gamma$-dichlorohydrin might be interchangeable with its $\alpha\beta$-isomeride, or alternatively that migration of a methyl ether group had occurred.   Both these hypotheses must be regarded on many grounds as highly improbable.[24]   A satisfactory solution of the difficulty has now been provided by the preparation of the true β-methyl ether of glycerol,[25] which was obtained by the hydro-

[22] H. Hibbert and N. M. Carter, $J. Amer. Chem. Soc.$, 1928, **50**, 3376; $A.$, 170.

[23] $J.$, 1925, **127**, 2735; $A.$, 1926, 153.

[24] J. B. Conant and O. R. Quayle, $J. Amer. Chem. Soc.$, 1923, **45**, 2771; $A.$, 1924, i, 7; A. Fairbourne and G. W. Cowdrey, $loc. cit.$; compare H. Hibbert, M. E. Platt, and N. M. Carter, $J. Amer. Chem. Soc.$, 1929, **51**, 3644.

[25] H. S. Hill, M. S. Whelen, and H. Hibbert, $J. Amer. Chem. Soc.$, 1928, **50**, 2238; $A.$, 1928, 1213.

lysis of $\alpha\gamma$-benzylidene glycerol β-methyl ether, and by the subsequent proof that the compound isolated by Gilchrist and Purves was in fact the β-ether and not, as they supposed, the α-derivative.[26] Useful confirmation is thus given of conclusions reached by H. Hibbert, M. S. Whelen, and N. M. Carter [27] to the effect that the methyl ethers of glycerol and other polyhydric alcohols are stable substances which display no liability to isomerise by migration of methyl groups and therefore are eminently suitable for use as reference compounds.

Of other methylated glycerols required as reference compounds, the α-monomethyl ether and the $\alpha\beta\gamma$-trimethyl ether [28] clearly have the structures ascribed to them, but there is some confusion in the literature concerning the two dimethyl ethers. A supposed $\alpha\beta$-dimethyl ether was prepared by Gilchrist and Purves by the action of sodium methoxide on glycerol $\alpha\gamma$-dichlorohydrin. These authors believed that isomerisation took place during the reaction, but a repetition [29] of their work has shown that their product is identical with the $\alpha\gamma$-dimethyl ether of glycerol prepared by Zunino.[30]

The reaction between the chlorohydrin and sodium methoxide therefore follows a normal course without involving isomerisation, and the important conclusion may be drawn that the chlorohydrins, so far from being unsuitable initial materials for the preparation of glycerol ethers, can be made to yield at will either α- or β-ethers. By taking advantage of this discovery it may be anticipated that the true glycerol $\alpha\beta$-dimethyl ether required to complete the series of reference compounds will be obtainable by the methylation and subsequent hydrolysis of glycerol α-monochlorohydrin.[31]

It is of interest that ethers of glycerol occur in nature, forming a link between the fats and the waxes. Batyl alcohol, which occurs in the liver of certain elasmobranch fish, along with selachyl alcohol and squalene, has been shown to be either the α- or the β-monoglyceryl ether of octadecyl alcohol, having one or other of the following structures :

(I.) $C_{18}H_{37}{\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ $C_{18}H_{37}{\cdot}O{\cdot}CH(CH_2{\cdot}OH)_2$ (II.)
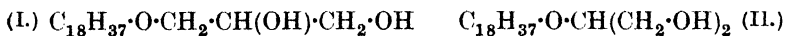
Treatment of batyl alcohol with hydriodic acid gives crystalline octadecyl iodide, the identity of which was confirmed by its trans-

[26] A. Fairbourne, *J.*, 1929, 2232; *A.*, 1422.

[27] *J. Amer. Chem. Soc.*, 1929, **51**, 302; *A.*, 292.

[28] J. C. Irvine, J. L. A. Macdonald, and C. W. Soutar, *loc. cit.*; H. G. Gilchrist and C. B. Purves, *loc. cit.*

[29] A. Fairbourne, *J.*, 1929, 1151; *A.*, 1038.

[30] *Atti R. Accad. Lincei*, 1897, **6**, 348; *A.*, 1899, i, 410.

[31] A. Fairbourne, *J.*, 1929, 2234; *A.*, 1422.

formation into octadecyl alcohol. The second of the two possible formulæ is favoured by the authors [32] on account of the ease with which the diacetyl derivative and the phenylurethane of batyl alcohol are formed.

Since batyl alcohol is the saturated dihydro-derivative of selachyl alcohol, the latter substance, which gives nonoic acid on oxidation with potassium permanganate, can be represented by a formula similar to one of the above but with the oleyl group,

$$CH_3 \cdot [CH_2]_7 \cdot CH\!:\!CH \cdot C_8H_{16},$$
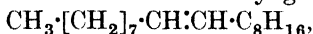
in place of $C_{18}H_{37}$.

Structure of the Quadrivalent Derivatives of Tellurium.

Few instances are known in which the existence of isomerism among quadrivalent compounds of an element requires the postulation of a planar distribution of the four valencies and a *cis*- and *trans*-arrangement of the addenda. Up to the present the compounds of quadrivalent tellurium and platinum have been the chief of these, the evidence in the case of tellurium resting mainly on the work of Vernon,[33] who obtained two forms of dimethyltelluronium di-iodide and of the corresponding base. Similar results were obtained with the dibromide and the dichloride and two distinct series of substances were recognised, designated respectively α- and β-, the isomerism of which was explained by means of the *cis–trans* arrangements of groups shown in the plane formulæ (I) and (II).

$$\underset{Me}{\overset{I}{>}}Te\underset{I}{\overset{Me}{<}} \qquad\qquad \underset{Me}{\overset{Me}{>}}Te\underset{I}{\overset{I}{<}}$$
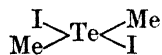
(I.) α-Di-iodide.   (II.) β-Di-iodide.

Such a case was clearly exceptional and a re-examination of the whole problem by H. D. K. Drew [34] has resulted in an important paper, in which it is shown that corresponding compounds of the α- and β-series are not stereoisomeric but are structurally different. The α-compounds are of the normal type and in these tellurium has in all probability a tetrahedral valency distribution. Tellurium, therefore, ceases to be an exception to the general rule of the tetrahedral distribution of valencies. Compounds of the β-series are, on the other hand, complex salt-like substances which are polar in character in contrast with the broadly non-polar nature of the α-substances. Similar general conclusions may be held to apply to the ethyl and other homologues.

Vernon's β-base is a mixed anhydride of formula $TeMe_3 \cdot O \cdot TeMeO$,

[32] I. M. Heilbron and W. M. Owens, *J.*, 1928, 943; *A.*, 1928, 616.

[33] R. H. Vernon, *J.*, 1920, **117**, 86, 889; 1921, **119**, 687; (Miss) I. E. Knaggs and R. H. Vernon, *J.*, 1921, **119**, 105.

[34] *J.*, 1929, 560; *A.*, 546.

which gives on treatment with hydrogen iodide the easily separable substances $TeMe_3I$ and $MeTeO \cdot OH$. The latter is readily converted by an excess of hydrogen iodide into methyltelluronium tri-iodide, $TeMeI_3$, which in turn readily combines with $TeMe_3I$ to give Vernon's β-di-iodide, $TeMe_3I \cdot TeMeI_3$. Experiments with the corresponding bromides and mixed β-dihalides containing both bromine and iodine have led to the view that the constitution of the salts can be most correctly represented by the general formula $Me_3\overset{+}{Te} \ldots \ldots \overset{-}{Te}MeX_4$, corresponding to the co-ordination formula $[Me_3Te]TeMeX_4$, where all the halogens and alkyl groups are linked covalently with tellurium. Support for this is found in the fact that the β-di-iodide and potassium iodide give, in acetone solution, trimethyltelluronium iodide and a substance which is probably the salt $[TeMeI_4]K$. On dissociation by moisture the latter yields potassium iodide and methyltelluronium tri-iodide.

The conversion of the α- into the β-base must involve the wandering of a methyl group from one tellurium atom to another and it is suggested by Drew that this may take place through the anhydride, $HO \cdot TeMe_2 \cdot O \cdot TeMe_2 \cdot OH$ (A), which gives the β-base as the result of a molecular re-arrangement similar to the pinacol–pinacolin transformation :

$$(A) \longrightarrow Me_2Te{<}^{O}_{O}{>}TeMe_2 \longrightarrow Me_3Te-O-TeMeO$$
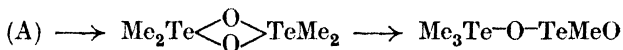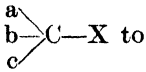
In the course of earlier work on the properties of quadrivalent tellurium compounds T. M. Lowry and F. L. Gilbert [35] extended Vernon's observations to the corresponding diethyl derivatives and seemed to favour the view of the non-equivalence of the coplanar halogen–tellurium valency linkings. They now accept Drew's main conclusions, for which they find additional support in the results of an extensive series of physico-chemical measurements,[36] but consider that the contrast between the α- and β-compounds is not sufficient to identify the β-salts as necessarily containing always the complex ion and the α-salts as invariably monomeric.

The Walden Inversion.

Although many hypotheses have been advanced to explain the mechanism of the Walden inversion, it is unfortunately the case that none of them will account adequately for all the facts. In one of the more recent attempts to evolve a general theory a suggestion is made that the result is dependent on the reaction distance B—Y

[35] *J.*, 1928, 307, 1997, 3179; *A.*, 1928, 349, 1098; 1929, 179.
[36] *J.*, 1929, 2076; *A.*, 1218.

in the molecule BY which reacts with the molecule $b{-}\!\!\overset{a\diagdown}{\underset{c\diagup}{{>}}}\!\!C{-}X$ to
give CabcY.   If the length B—Y is large compared with C—X, then inspection of models shows that rearrangement is likely to occur and the reaction will be accompanied by inversion.[37]   It is difficult, however, to account on this basis for phenomena such as the influence of the solvent.

A new method of approach to the problem is being explored by H. N. K. Rördam,[38] who has advanced a reaction mechanism which is susceptible to mathematical treatment and is capable, therefore, of being tested quantitatively.   The reacting molecule (I) is supposed, in the first stage, to split off the group E.

(I.)
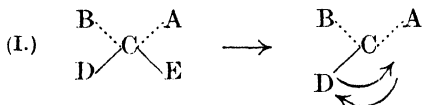
Owing to the disturbance, oscillation then begins in the directions indicated by the arrows and the incidence of a Walden inversion depends on whether the entering ion or radical X takes up its position when D is on the right or left of the plane ACB.   If the time of oscillation and the concentrations and activities of the components be known, it is possible to found a quantitative theory and to predict the amount of inversion which will take place in a given reaction.   With the aid of Brönsted's equation for reaction velocities the equation finally obtained is $n = kC'_x f_l f_x / f_{lx}$, in which n is the fraction of the reaction product retaining the original configuration, C_x is the mean concentration of X at the beginning and the end of the reaction, $f_l, f_x,$ and f_{lx} are the activity coefficients of the oscillating molecule, of X, and of the resulting compound, respectively. The activity coefficients are not known directly, but certain probable assumptions are made concerning them.

From the point of view of the oscillation hypothesis two distinct types of reaction are to be expected.   Reactions of type I involve the splitting of the optically active molecule either spontaneously or by the action of some molecule which is neither identical with nor contains the entering radical.   This type includes the reaction between bromosuccinic acid and the xanthogenates [39] and also all reactions where halogen linked to an asymmetric atom is replaced by hydroxyl or other ions or under the influence of such ions.   To all such reactions the theory indicated above applies, and in all cases where sufficiently accurate experimental data are available the

[37] B. Holmberg, Ber., 1926, 59, [B], 125; A., 1926, 384.
[38] J., 1928, 2447; 1929, 1282; A., 1928, 1215; 1929, 1041.
[39] B. Holmberg, loc. cit.

agreement between theory and experiment is good. The conception of the Walden inversion here advocated leads to the conclusion that, in reactions of type I, that form of the reaction product which increases in amount with increasing concentration of the entering radical possesses the same configuration as the original substance. It may be possible, therefore, to use this method as a means of deciding which forms of related substances have similar configurations, and, in view of the great importance of the latter problem and the state of confusion in which it has rested, the further development of Rördam's work will be awaited with much interest.

The second type of reaction considered by this author comprises that in which the splitting of the active molecule is caused directly by the molecule containing the entering radical. Possibly an additive compound is formed and, since in that case the entering radical must always be at very nearly the same distance from the vacant position on the asymmetric atom, replacement can be expected to occur only at one phase of the oscillation. Inversion may, or may not, occur, depending on the structure of the molecules and the period of oscillation, but as all the factors have constant values, only one stereoisomeric form of the product is to be expected. To such reactions the theoretical treatment outlined above cannot be applied. As examples the following may be cited : the replacement of hydroxyl groups by halogen by means of phosphorus pentachloride, thionyl chloride, or nitrosyl bromide. In certain special cases (the action of nitrosyl bromide on active amino-compounds) it is possible that a transition stage between types I and II is to be found.

The more restricted problem of determining at what stage in a series of reactions a Walden inversion takes place continues to engage much attention. The difficulty here lies in the lack of methods for correlating the configurations of different compounds; for when an optically active substance is transformable at will into oppositely rotating forms of the same reaction product it is rarely possible to say more than that a Walden inversion has taken place in one of the reactions. R. Kuhn and T. Wagner-Jauregg [40] now propose for the elucidation of configuration a novel method which is not dependent on the comparison of optical properties, and by means of which they have worked out the relationships in the series comprising tartaric acid, malic acid, and the halogenated succinic acids. They have shown,[41] in the first place, that in conformity with theory but contrary to the work of A. Sonn and W. Rosinsky,[42]

[40] *Ber.*, 1928, **61**, [*B*], 504; *A.*, 1928, 506.
[41] *Idem, ibid.*, p. 481; *A.*, 1928, 506.
[42] *Ibid.*, 1925, **58**, [*B*], 1688; *A.*, 1925, i, 1237.

there are four active chloromalic acids, the configurations of which have been ascertained by comparing the physical properties of the racemic forms with those of the r- and $meso$-forms of the dichloro- and dihydroxy-succinic acids. A similar comparison was instituted with the corresponding esters. The "$meso$-"structure (I) is ascribed to that dl-chloromalic acid the properties of which are on the whole intermediate between those of $meso$dichloro- and $meso$-dihydroxy-succinic acids, and the "rac" structure (II) to the dl-chloromalic acid with properties intermediate between those of r-dichloro- and r-dihydroxy-succinic acids.

$$
\begin{array}{cc}
\text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{H·C·OH} & \text{HO·C·H} \\
\text{H·C·Cl} & \text{Cl·C·H} \\
\text{CO}_2\text{H} & \text{CO}_2\text{H} \\
l\text{-chloro-} & d\text{-chloro-} \\
d\text{-hydroxy-} & l\text{-hydroxy-}
\end{array}
\qquad
\begin{array}{cc}
\text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{H·C·OH} & \text{HO·C·H} \\
\text{Cl·C·H} & \text{H·C·Cl} \\
\text{CO}_2\text{H} & \text{CO}_2\text{H} \\
d\text{-chloro-} & l\text{-chloro-} \\
d\text{-hydroxy-} & l\text{-hydroxy-}
\end{array}
$$

(I.) Chloromalic acid.   (II.) Chloromalic acid.
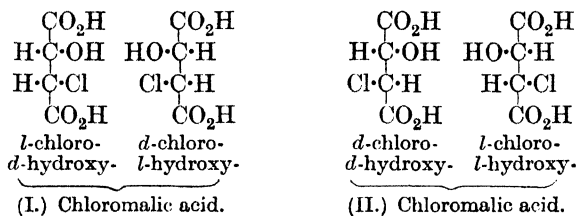
The dextrorotatory form of chloromalic acid (I) is thus regarded as composed of a half-molecule of l-tartaric acid and a half-molecule of d-dichlorosuccinic acid and, since the latter is dextrorotatory (see below), it follows that the sign of rotation of the chloromalic acids is governed by the position of the halogen atom.

The relationship of the chlorosuccinic acids to $d(+)$-malic acid, to which all stereochemical formulæ are referred, is determined in the following way. It is supposed that a halogen atom is introduced

$$
\begin{array}{ccc}
\text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{H·C·H} & \text{Cl·C·H} & \text{H·C·Cl} \\
\text{H·C·OH} & \text{H·C·OH} & \text{H·C·OH} \\
\text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{(I.)} & \text{(II.)} & \text{(III.)}
\end{array}
$$
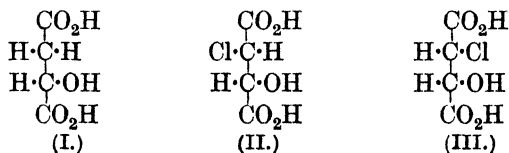
into (I), which already contains the hydroxyl group of $d(+)$-malic acid. The halogen may be introduced in either of two ways, making the upper carbon atom either d- or l-. The compounds so formed may be referred to as $\left(\dfrac{d}{D}\right)$ and $\left(\dfrac{l}{D}\right)$ respectively, where small letters refer to the dissymmetric centre to which the halogen is attached, and capital letters refer to the centre to which the hydroxyl group is joined. Now the first of these chloromalic acids $\left(\dfrac{d}{D}\right)$ must be intermediate, in the totality of its physical properties, between the compounds $\left(\dfrac{D}{D}\right)$, $i.e.$, tartaric acid, and $\left(\dfrac{d}{d}\right)$, $i.e.$, d-dichlorosuccinic

acid. Similarly the second chloromalic acid $\left(\dfrac{l}{D}\right)$ must lie between

mesotartaric acid $\left(\dfrac{L}{D}\right)$ and mesodichlorosuccinic acid $\left(\dfrac{l}{d}\right)$. All the

comparisons of physical properties can be made with the racemic forms of the acids. Since the configuration of the inactive chloromalic acids has been established and the position of the hydroxyl groups in the active chloromalic acids has been determined by their conversion into malic acids (see above), it is possible to decide at once whether Walden inversion occurs during the transformation of d-tartaric acid into chloromalic acid. For example, methyl dl-mesochloromalate, which occupies an intermediate position between (IV) and (VI), is converted into methyl r-dichlorosuccinate (VII) on treatment with thionyl chloride. Direct replacement

$$
\begin{array}{ccccc}
\begin{array}{l}|Cl\\|Cl\end{array} & \begin{array}{l}|Cl\\|OH\end{array} & \begin{array}{l}|OH\\|OH\end{array} & \begin{array}{l}Cl|\\\ \ |Cl\end{array} & \begin{array}{l}HO|\\\ \ \ \ \ |OH\end{array}\\
\text{(IV.)} & \text{(V.)} & \text{(VI.)} & \text{(VII.)} & \text{(VIII.)}
\end{array}
$$
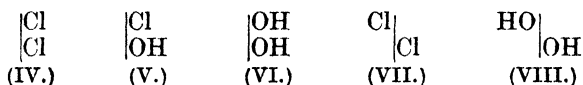
would have involved the conversion of (V) into the meso-form (IV), and it follows that a Walden inversion has taken place. Similarly ethyl d-tartrate (VIII) yields the " meso "-chloromalic ester (V) by the action of thionyl chloride in pyridine solution, and here again inversion must have occurred. There is, therefore, a double inversion during the passage of d(+)-tartaric acid into lævorotatory dichlorosuccinic acid, which must in consequence belong to the l-series and should be termed l(−)-dichlorosuccinic acid. Although direct conversion of an active dichloro- into a monochloro-succinic acid could not be accomplished, a comparison of the rotations of the acids and of their esters under various conditions as to solvent and temperature leads to the conclusion that (−)-monochlorosuccinic acid is configuratively related to the l(−)-dichloro-acid. The following cycle of transformations therefore involves inversion during the reaction with phosphorus pentachloride but not during that with silver oxide. It will be noted that with respect to the configuration of (+)-chlorosuccinic acid the results are opposed to those of G. W. Clough,[43] whose fundamental postulate is criticised.

$d(+)$-Chlorosuccinic acid

$l(−)$-Malic acid $d(+)$-Malic acid

$l(−)$-Chlorosuccinic acid
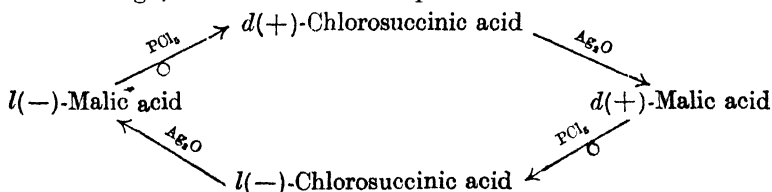
[43] J., 1915, 107, 1509; 1918, 113, 526; 1926, 1674; A., 1915, ii, 811; 1918, ii, 255; 1926, 937.

In the same paper many transformations in the maleic–fumaric acid series are described, accurate quantitative data being given. It is found, for example, that addition of hypochlorous acid to fumaric acid occurs mainly (80%) in the *trans*-position and that chloromaleic acid is formed from *meso*chloromalic acid by a process involving *trans*-elimination of water and molecular transformation. Contrary to the results of E. M. Terry and L. Eichelberger,[44] sodium fumarate gives more than 80% of *meso*dichlorosuccinic acid by the addition of chlorine in the presence of sodium chloride.

Additive reactions at an ethenoid bond have been studied from the point of view of energy relationships,[45] the examples chosen being the hydrogenation of the sodium salts of dimethyl-fumaric and -maleic acids in aqueous solution and the hydrogenation of the stereoisomeric βγ-diphenyl-Δβ-butenes in various solvents. Homogeneous addition is the exception rather than the rule and often, by suitable choice of conditions and reaction velocity, *cis*- or *trans*-addition may be made to predominate at will. The course of the addition process is controlled by the differences in energy of the products and of the *cis*- and *trans*-initial materials, and by the rate of addition.

Returning to the question of the configurational relationships, K. Freudenberg and L. Markert [46] have attempted to determine the configuration of the α-bromopropionic acids by comparison of the optical behaviour of the esters, chlorides, and substituted amides with the corresponding compounds of *d*-methoxy-, acetoxy-, benzoyloxy- and *p*-toluenesulphonyloxy-propionic acid. On the assumption that analogous compounds of similar configuration suffer corresponding rotational displacements when subjected to the same changes, it is deduced from the experimental results that the lævorotatory α-bromopropionic acid is related to *l*(−)-malic acid. Similarly, a comparison of optical properties indicates that (−)-bromosuccinic acid belongs to the *l*-series. In conjunction with the work of R. Kuhn and T. Wagner-Jauregg (see above), these and earlier results enable K. Freudenberg and A. Lux [47] to regard the following series as definitely established : *l*(+)-lactic acid, *l*(−)-halogeno-propionic acids, *l*(+)-alanine, *l*(−)-malic acid, *l*(−)-halogeno-succinic acids, and *l*(+)-aspartic acid. A review of the experimental data leads to the conclusion that Clough's method is trustworthy within particular groups, but may break down when substances belonging to different groups are compared.

[44] *J. Amer. Chem. Soc.*, 1925, **47**, 1067; *A.*, 1925, i, 631.

[45] E. Ott, R. Schröter, and A. Behr, *Ber.*, 1928, **61**, [B], 2124; *A.*, 1928, 1350.

[46] *Ber.*, 1927, **60**, [B], 2447; *A.*, 1928, 154.

[47] *Ber.*, 1928, **61**, [B], 1083; *A.*, 1928, 735.

Freudenberg and Kuhn agree, therefore, in regarding (+)-halogenosuccinic acids as configuratively related to the (+)-hydroxyacids, but such a view does not as yet command universal acceptance. It is at variance with Clough's opinions and as the result of extensive investigations concerning the inter-relationship of nitromalic, aspartic, and malic acids B. Holmberg [48] has come to the conclusion that the dextrorotatory halogenosuccinic acids belong to the same series as *l*-malic acid, a view which is shared also by P. A. Levene and H. L. Haller.[49] With regard to natural *l*(+)-aspartic acid the opinion of Holmberg coincides with that of K. Freudenberg and A. Noë.[50]

Similar problems are met with in connexion with the relative configurations of optically active secondary alcohols. For instance, dextrorotatory β-octanol is converted into lævorotatory halides by the action of hydrogen chloride, bromide, or iodide or by thionyl chloride or bromide. The occurrence of a Walden inversion is not necessarily implied by this change in sign of rotation and contrary opinions have been held on this point. Basing their views on a comparison of optical properties, R. H. Pickard and J. Kenyon [51] believed that (+)-β-octanol was configuratively related to the (+)-β-halides, whereas P. A. Levene and L. A. Mikeska,[52] as the result of somewhat insecure arguments derived from the observed reversal of sign of rotation during the change $C_8H_{17}\cdot SH \longrightarrow C_8H_{17}\cdot SO_3H$ (where configurational change cannot occur), considered that the (+)-β-octanol and the (—)-β-halides had similar configurations.

The problem has now been investigated by two chemical methods [53] which serve to establish more definitely the configurational relationships, the underlying principle being the conversion, by closely similar means, of a derivative of the optically active alcohol into (a) the alcohol or a carboxylic ester of the alcohol, and (b) a halide. It is assumed that (a) and (b) then have the same configuration, since they are produced under similar conditions by reactions of the same type. If the configuration of the derivative employed is known, the occurrence of a Walden inversion in one of the reactions is at once detectable.

The above conditions are realised in the present instance because *d*-β-octanol can be converted into *d*-β-octyl *dl*-*p*-toluenesulphinate and *p*-toluenesulphonate without change in configuration. When

[48] *Ber.*, 1928, **61**, [*B*], 1885; *A.*, 1928, 1216.
[49] *J. Biol. Chem.*, 1929, **83**, 185; *A.*, 1041.
[50] *Ber.*, 1925, **58**, [*B*], 2399; *A.*, 1926, 53.   [51] *J.*, 1911, **99**, 45.
[52] *J. Biol. Chem.*, 1924, **59**, 473; *A.*, 1924, i, 940.
[53] A. J. H. Houssa, J. Kenyon, and H. Phillips, *J.*, 1929, 1700; *A.*, 1164.

treated with potassium acetate, d-β-octyl p-toluenesulphonate gives lævorotatory β-octyl acetate. This change must involve a Walden inversion, because d-β-octanol gives a dextrorotatory acetate when treated with acetic anhydride. A similar conclusion is drawn from the fact that the d-p-toluenesulphonate gives with lithium chloride a lævorotatory β-chloro-octane.

The experimental results obtained with d-β-octyl dl-p-toluenesulphinate are summarised in the following scheme :

$$\underset{(+)}{\underset{CH_3}{\overset{C_6H_{13}}{>}}C\underset{O\cdot SO\cdot C_7H_7}{\overset{H}{<}}} \begin{array}{c} \xrightarrow{\text{HOOl}} \underset{(-)}{\underset{CH_3}{\overset{C_6H_{13}}{>}}C\underset{H}{\overset{OH}{<}}} + C_7H_7\cdot SO_2Cl \\ \\ \xrightarrow{Cl_2} \underset{(-)}{\underset{CH_3}{\overset{C_6H_{13}}{>}}C\underset{H}{\overset{Cl}{<}}} + C_7H_7\cdot SO_2Cl \end{array}$$
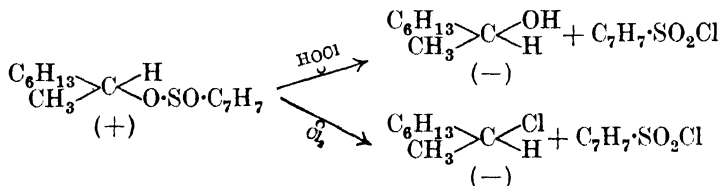
The formation of l-β-octanol shows conclusively that a Walden inversion has occurred, since d-β-octyl dl-p-toluenesulphinate has the same configuration as d-β-octanol, and the reaction with chlorine must be regarded as involving a similar inversion.

These transformations are of special interest in connexion with the mechanism of the Walden inversion. Since the p-toluene-sulphinoxy-radical can be represented by the formula (I), it is suggested that the reaction with chlorine proceeds *via* the inter-mediate complex (II), which dissociates with rupture of the C·O

$$\text{(I.)} \quad \underset{\underset{+}{\overset{\times\times}{}}}{\overset{\overset{-}{O}}{\underset{}{-O\overset{\times\cdot}{\times}\overset{}{S}\overset{\times}{\cdot}C_7H_7}}} \qquad\qquad \underset{\underset{\overset{-}{Cl}\quad \overset{\times\cdot}{Cl}}{}}{\overset{C_6H_{13}}{\underset{CH_3}{>}}C\underset{O\overset{\times}{\times}\overset{\cdot ++}{S}\overset{\times}{\cdot}C_7H_7}{\overset{H}{<}}} \quad \text{(II.)}$$
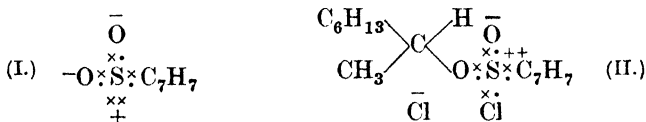
bond, leaving a carbonium ion. Inversion may take place before the addition of the chlorine ion or, alternatively, if dissociation and addition occur simultaneously, the latter may take effect on the opposite side of the asymmetric complex.[54]

Inasmuch as the following series of reactions has been carried out, it follows that treatment of the halides with silver oxide must involve inversion, and it is suggested by Houssa, Kenyon, and Phillips that " far from being a comparatively rare phenomenon, inversion occurs whenever a group attached to an asymmetric

$$\underset{d\text{-}}{\underset{CH_3}{\overset{C_6H_{13}}{>}}C\underset{OH}{\overset{H}{<}}} \xrightarrow{\text{HBr}} \underset{l\text{-}}{\underset{CH_3}{\overset{C_6H_{13}}{>}}C\underset{H}{\overset{Br}{<}}} \xrightarrow{\text{Ag}_2O} \underset{d\text{-}}{\underset{CH_3}{\overset{C_6H_{13}}{>}}C\underset{OH}{\overset{H}{<}}}$$
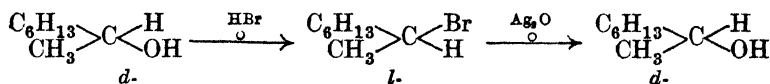
carbon atom is replaced, unless a phenyl group is directly linked to the asymmetric carbon atom or a carboxyl group is present in the

[54] Compare T. M. Lowry, *Deuxième Conseil de Chimie Solvay*, 1925, 40.

molecule., These disturbing factors may, however, lead to the occurrence of two inversions during the replacement."

Attention is directed also to a series of papers by P. A. Levene and H. L. Haller, in which the configurational relationships of various carbinols are discussed. The subjects treated include the butan-γ-ols and pentan-δ-ols,[55] methylethyl- and ethyl-n-propyl-carbinols,[56] α-hydroxyvaleric acid,[57] hexan-β-ol and α-hydroxy-n-hexoic acid,[58] methylpropylcarbinol,[59] n-pentan-β-ol,[60]   ζ-methylheptan-β-ol,[61] heptan-γ-ol and octan-δ-ol.[62]

In view of the recent tendency to regard replacements of groups attached to asymmetric carbon atoms as being normally accompanied by inversion it is of interest to recall the suggestion that the ribose obtainable from nucleic acids may be derived from xylose-3-phosphoric acid by inversion during hydrolysis.[63] Although the evidence in this particular case is inconclusive,[64] certain transformations in the hexose series have been described which favour the view that under suitable conditions such an inversion may occur. It is claimed [65] that α-fructose-diacetone-3-phosphoric acid is convertible into a crystalline anhydrohexosazone which is not identical with the osazone of Fischer and Zach's 3 : 6-anhydroglucose,[66] and the suggestion is made that an anhydroallose derivative is formed as the result of a Walden inversion during the removal of the phosphoric acid group. The same osazone is apparently formed from glucose-diacetone-3-phosphoric acid. On the other hand, the phosphoric ester of β-fructose-diacetone gave ordinary glucosazone. Until a better understanding of the mechanism of these complex reactions is forthcoming it would be unwise to accept the results as indicating the possibility of inversion during the ordinary hydrolysis of phosphoric esters. Under the usual conditions this is held to be unlikely, and experiments have shown that the product obtained by hydrolysing the diphosphate of l-glyceric acid is optically pure.[67] Inversion is to be expected only when the

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[55] J. Biol. Chem., 1927, 72, 591 ; A., 1927, 643.

[56] Ibid., 1928, 76, 415 ; A., 1928, 394.

[57] Ibid., 1928, 77, 555 ; A., 1928, 737.

[58] Ibid., 1928, 79, 475 ; A., 1928, 1353.

[59] Ibid., 1929, 81, 425 ; A., 424.

[60] Ibid., 1929, 81, 703 ; A., 540.

[61] Ibid., 1929, 83, 117 ; A., 1038.

[62] Ibid., p. 579 ; A., 1266.

[63] R. Robinson, Nature, 1927, 120, 44, 656 ; A., 1927, 960, 1225.

[64] P. A. Levene and R. Mori, J. Biol. Chem., 1929, 81, 215 ; A., 297.

[65] P. A. Levene, A. L. Raymond, and A. Walti, ibid., 1929, 82, 191 ; A., 683 ; A. L. Raymond and P. A. Levene, ibid., 1929, 83, 619 ; A., 1278.

[66] Ber., 1912, 45, 456 ; A., 1912, i, 239.

[67] S. Posternak and T. Posternak, Helv. Chim. Acta, 1929, 12, 1168.

conditions of reaction are such that the C–O linking is ruptured, and in this connexion reference may be made to the observations of J. Kenyon, H. Phillips, and H. G. Turley [68] on the removal of the p-toluenesulphonyloxy-group from an optically active molecule. According to these authors the direct hydrolysis of the sodium salt of l-α-p-toluenesulphonyloxypropionic acid with sodium hydroxide proceeds without rupture of the C·O bond and without inversion, whereas the interaction of potassium benzoate and ethyl l-α-p-toluenesulphonyloxypropionate involves the rupture of this bond and leads to complete inversion.
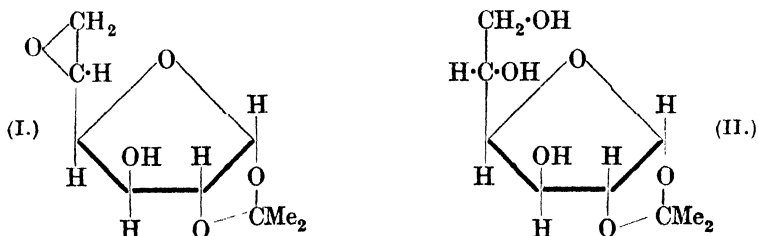
Another case of a Walden inversion in the hexose series is provided by the reported formation of d-idose-monoacetone (II) when the monoacetone derivative of 5 : 6-anhydroglucose (I) is treated with sodium hydroxide.[69] The conversion is only partial, and glucose-monoacetone is produced simultaneously, whilst ammonia appears to open the ethylene oxide ring almost entirely in one direction, giving 6-aminoglucose-monoacetone. The inversion may be presumed to arise from the scission of the ethylene oxide ring at the bond which unites the fifth carbon atom to the oxygen of the ring.

Natural Products Allied to the Open-chain Terpenes.

Squalene.—Progress continues to be made in the study of the hydrocarbon squalene, which occurs, along with sterol, selachyl alcohol, and batyl alcohol, in the unsaponifiable matter from the oils of elasmobranch fish. The formulation of squalene as a dihydrotriterpene, $C_{30}H_{50}$, may now be considered as settled,[70] since under all methods of attack the substance yields products which are typical of those to be expected in the terpene series. Constant-boiling mixtures of mono- and di-hydromonoterpenes are obtained when squalene is heated under diminished pressure in a current of nitrogen. The action of ozone yields a hexaozonide, which is decomposed by water, giving lævulic, succinic, and formic acids,

[68] *J.*, 1925, **127**, 399; *A.*, 1925, i, 507.

[69] H. Ohle and L. von Vargha, *Ber.*, 1929, **62**, [*B*], 2435; *A.*, 1279.

[70] I. M. Heilbron, W. M. Owens, and I. A. Simpson, *J.*, 1929, 873; *A.*, 789; I. M. Heilbron and A. Thompson, *ibid.*, p. 883; *A.*, 790.

acetone and its peroxide, formaldehyde, carbon dioxide, lævulaldehyde peroxide, and a complex peroxide of methylheptenone. Oxidation in acetone solution by solid potassium permanganate gives succinic acid, methylheptenone, and dihydro-ψ-ionone. These results prove that the carbon skeleton $\underset{C \cdot C \vdots C \cdot C \cdot C \cdot C \vdots C \cdot C \cdot C \vdots C \vdots}{\overset{\text{C} \qquad \text{C} \qquad \text{C}}{}}$ is present in squalene. The production of formaldehyde and acetaldehyde, in the oxidation of the hydrocarbon by chromyl chloride, reveals the presence of both the $>C \vdots CH_2$ and the $CMe \vdots CHMe$ groups, as does also the formation of carbon dioxide, formaldehyde, formic acid, and succinic acid in the same decomposition (see above). It is suggested, therefore, that the squalene exists as a mixture of at least two isomerides, to which the formulæ (I) and (II) are ascribed.

$$(a)$$

(I.) (b) $\underset{CH \cdot [CH_2]_2 \cdot CMe \vdots CH \cdot [CH_2]_2 \cdot CMe \vdots CH \cdot [CH_2]_2 \cdot CMe \vdots CHMe}{CMe \cdot [CH_2]_2 \cdot CH \vdots CMe \cdot [CH_2]_2 \cdot CH \vdots CMe_2}$

$\longleftarrow \cdots \cdots \cdots \text{acid } C_{17}H_{34}O_2 \cdots \cdots \longrightarrow$

(II.) $CMe_2 \vdots CH \cdot CH_2 \cdot [CH_2 \cdot C(\vdots CH_2) \cdot CH_2 \cdot CH_2]_4 \cdot CH_2 \cdot CMe \vdots CHMe$.
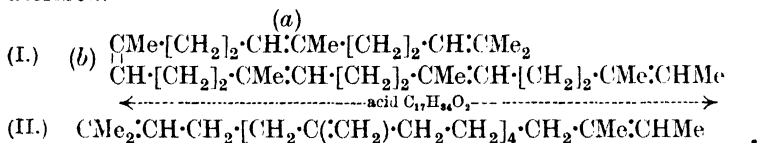
Very satisfactory confirmation of these views has been obtained by hydrogenating squalene to a point corresponding to the decahydro-derivative and submitting the product to ozonolysis. It appears that the hydrogenation is selective, giving isomeric decahydrosqualenes along with some squalane (dodecahydrosqualene) and products less hydrogenated. The substances isolated after the treatment with ozone include the following : methyl isohexyl ketone, hexahydro-ψ-ionone ($CHMe_2 \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot COMe$), a ketone $C_{19}H_{38}O$ (probably 3 : 7 : 11-trimethylhexadecan-15-one), γ-methyl-n-valeric acid, 4 : 8-dimethylnonoic acid, and an acid $C_{17}H_{34}O_2$ (probably 3 : 7 : 11-trimethyltetradecoic acid). The isolation of the first two of these substances establishes the presence of double bonds at (a) and (b) in (I) and the formation of the acid $C_{17}H_{34}O_2$ is readily explicable. It is more difficult, however, to account for the formation of the other two acids and for the ketone $C_{19}H_{38}O$, and it seems most unlikely that either (I) or (II) could yield these substances either directly or indirectly under the given experimental conditions. The authors are forced to conclude that squalene exists also in a third stable form (III) :

$\longleftarrow \text{———} C_{17}H_{32}O_2 \text{ acid} \text{———} \longrightarrow$

(III.) $\underset{CMe \cdot [CH_2]_2 \cdot CH \vdots CMe \cdot [CH_2]_2 \cdot CH \vdots CMe \cdot [CH_2]_2 \cdot CMe \vdots CHMe}{CH \cdot [CH_2]_2 \cdot CMe \vdots CH \cdot CH_2 \cdot CH \vdots CMe_2}$

$\longleftarrow \text{———} C_{19}H_{38}O_2 \text{ ketone} \text{———} \longrightarrow$
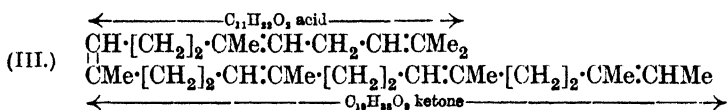
Consideration of the acids and ketones produced leads to the idea that the addition of hydrogen proceeds from the terminal group

CMe:CHMe, which is common to all three isomeric forms, since only in this way is it possible to explain the absence of ketones of higher molecular weight than hexahydro-ψ-ionone from (I) and of acids more complex than 4 : 8-dimethylnonoic acid from (III).

Bixin.—Considerable interest is being shown in the chemistry of bixin, a natural colouring matter obtained from the seeds of *Bixa orellana* and similar in many ways to crocetin and carotin. The formula $C_{24}H_{27}O_3 \cdot OMe$ now appears to be established,[71] although some workers still favour the formula $C_{26}H_{30}O_4$.[72] According to P. Karrer the special properties of bixin and crocetin and many other natural products are due to the presence of a series of conjugated double linkings. Bixin very readily yields *m*-xylene when heated, but the pre-existence of a benzene nucleus in the molecule is most unlikely and the aromatic derivative is probably formed by scission and rearrangement of the conjugated double bonds.[73] The

presence of a five-membered ring, $CH\underset{\displaystyle CH=C^-}{\overset{\displaystyle CMe-C^-}{<}}$, has been suggested

in order to account for the intense colour, but this assumption does not seem to be necessary, and from a study of the dibasic acid norbixin, $C_{24}H_{28}O_4$ (obtained from bixin by alkaline hydrolysis), Karrer and his collaborators have obtained evidence in support of the structure $CO_2Me \cdot CH:[CH \cdot CMe:CH \cdot CH:]_4CH \cdot CO_2H$ for bixin, suggested by Kuhn on the basis of Karrer's work on the structure of crocetin.[75] It will be seen that the molecule is composed of four isoprene and two glyoxylic acid residues. Bixin readily undergoes isomerisation, probably geometric in nature.

Carbohydrates.

That free sugars are not open-chain compounds but are cyclic in structure, corresponding to the pyranosides or simple glucosides, has been made evident by previous work. It is none the less important to supplement this evidence by the isolation of a true open-chain aldehyde form of a sugar and to institute a comparison of its properties with those of a heterocyclic normal sugar. This has been achieved [76] by the preparation of the crystalline 2 : 3 : 4 : 5 : 6-penta-acetyl glucose, which has a rotation nearly zero and gives a positive test with Schiff's reagent.

Studies of the mutarotation of galactose and of the change of

[71] P. Karrer, A. Helfenstein, Rose Widmer, and T. B. van Itallie, *Helv. Chim. Acta,* 1929, **12**, 741; *A.,* 1075.

[72] F. Faltis and F. Vieböck, *Ber.,* 1929, **62**, [B], 701; *A.,* 575.

[73] R. Kuhn and A. Winterstein, *Helv. Chim. Acta,* 1928, **11**, 427, 716; *A.,* 1928, 644, 869.

[74] F. Faltis and F. Vieböck, *loc. cit.*

[75] P. Karrer and H. Salomon, *Helv. Chim. Acta,* 1928, **11**, 513; *A.,* 1928, 644.

[76] M. L. Wolfrom, *J. Amer. Chem. Soc.,* 1929, **51**, 2188; *A.,* 1043.

volume of an aqueous solution of this sugar furnish evidence of the presence of more than the two pyranose forms.[77] It seems probable that the two γ- or furanose varieties exist side by side with the α- and β-galactopyranoses in water. In boiling pyridine the β-galacto-furanose appears to be present in the proportion of 23%. Measurement indicates that the mutarotation velocities of glucose, tetramethyl glucose, and lactose in water are similar, but in the presence of hydroxyl ions the reactions are catalysed at very different rates.

When glucose is degraded into simpler compounds the change may proceed in either of two ways : [78] (1) non-oxidation processes are characterised by the formation of C_3 chains and are preceded by a rearrangement of glucose into the labile furanose form. This procedure includes processes which give rise to methylglyoxal, acetaldehyde, and products based on these substances; (2) the processes depending on primary oxidation of glucose probably occur through the pyranose form, and this proceeds most readily at C_1, C_5, and C_6 and usually with acid reagents. An endeavour to imitate by chemical reagents the fermentation processes of a hexose or its phosphate has led to the study [79] of the graded oxidation of a β-fructose sulphate in the form of its diacetone derivative. With increasing amounts of oxygen supplied from potassium permanganate, the substance yields a dextrorotatory intermediate product, $CMe_2 \Big\langle {}^{O \cdot C(OH) \cdot CH_2 \cdot O \cdot SO_3 K}_{O \cdot CH \cdot CH(CO_2 K)_2}$, which is at its maximum when 6 atoms of oxygen are supplied. In addition, 15% of the original fructose derivative remains unchanged, 15% is oxidised to carbon dioxide and sulphuric acid, and about one-third is converted into 4 mols. of carbon dioxide and 1 mol. of the glycollic acid derivative $CO_2 K \cdot CH_2 \cdot O \cdot SO_3 K$. Hydrolysis of the above complex intermediate product with N-hydrochloric acid at 100° for $\frac{1}{2}$ hour yields acetone, sulphuric acid, methylglyoxal (75%), glycollic acid, and carbon dioxide. It would appear that the above intermediate product first loses its acetone residue and breaks down into the sulphuric ester of dihydroxyacetone, which then gives methylglyoxal and sulphuric acid. The mechanism of the fermentation process envisaged by Neuberg as proceeding by the intermediate formation of C_3 residues

[77] C. N. Riiber, J. Minsaas, and R. T. Lyche, *J.*, 1929, 2173; *A.*, 1427; T. M. Lowry and G. F. Smith, *J. Physical Chem.*, 1929, **33**, 9; *A.*, 272; H. H. Schlubach and V. Prochownick, *Ber.*, 1929, **62**, [*B*], 1502; *A.*, 912; T. M. Lowry and G. L. Wilson, *Trans. Faraday Soc.*, 1928, **24**, 683; *A.*, 36.

[78] K. Bernhauer and J. Nistler, *Biochem. Z.*, 1929, **205**, 230; *A.*, 543; K. Bernhauer, *ibid.*, 1929, **210**, 175; *A.*, 1167; M. Hönig and W. Ruzicka, *Ber.*, 1929, **62**, [*B*], 1434; *A.*, 910; F. Fischler, K. Täufler, and S. W. Souci, *Biochem. Z.*, 1929, **208**, 191; *A.*, 912; K. Bernhauer and K. Schön, *Z. physiol. Chem.*, 1929, **180**, 232; *A.*, 355.

[79] H. Ohle and J. Neuscheller, *Ber.*, 1929, **62**, [*B*], 1651; *A.*, 913.

is here imitated by chemical reagents. Some recent syntheses of hexose phosphates [80] have yielded preliminary results of interest although not of importance.

High yields of the monobasic acids derivable from sugars are promoted by conducting the oxidation with aqueous bromine in presence of calcium or barium benzoate.[81] The latter reagent removes the hydrogen bromide from the system and accelerates the oxidation, whilst preventing hydrolytic scission of products such as lactobionic acid. Products of the union of sugars with the alkaline-earth hydroxides have been studied more closely,[82] and their analyses show them to conform to definite proportions of sugar and alkaline earth.

Formulation of Sugars.—The projection formulæ introduced by Fischer have been of signal service for the expression of the configurations of sugars, but it was pointed out three years ago [83] that their extension to cyclic sugar formulæ has involved an error which can only be set right by a modification of the system. For example, the configuration of the groupings at C_5 in the glucose formula (I) is incorrectly formulated, since the ring closure from an open-chain to a cyclic form involves the rotation of the single linking between C_4 and C_5 through 120°. This has the effect of bringing the H at C_5 on the opposite side of the carbon chain and the result is correctly expressed in formula (II). The most satisfactory picture of the actual atom model of glucose is given by the perspective formula (III), which will doubtless enter into even more general use than is at present the case. The continued use of the expression (I) is transitional and a concession to the traditional utility of the Fischer system of expression.

β-Glucopyranose.
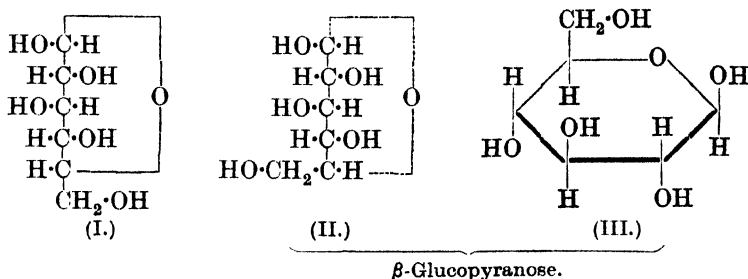
[80] B. Helferich and H. Du Mont, *Z. physiol. Chem.*, 1929, **181,** 300; *A.*, 683; A. L. Raymond and P. A. Levene, *J. Biol. Chem.*, 1929, **83,** 619; *A.*, 1278.

[81] C. S. Hudson and H. S. Isbell, *J. Amer. Chem. Soc.*, 1929, **51,** 2225; *Bur. Stand. J. Res.*, 1929, **3,** 57; *A.*, 1043; compare H. Kiliani, *Ber.*, 1929, **62,** [*B*], 588; *A.*, 541.

[82] J. E. Mackenzie and J. P. Quin, *J.*, 1929, 951; *A.*, 797.

[83] H. D. K. Drew and W. N. Haworth, *J.*, 1926, 2303; *A.*, 1926, 1125; see also *Ann. Reports*, 1926, **23,** 79.

Although a corresponding correction for all sugar forms was implied and has been used in the formulation of both the pyranose and the furanose type, yet a recent paper in the *Berichte* is devoted to a similar explanation applied to glucofuranose.[84] Doubtless this will serve a useful purpose in placing emphasis on the inadequacy of the Fischer convention (IV) as a complete mode of formulation of γ-glucose. Employment of either of the expressions (V) and (VI) will become more general as is the case with (II) and (III).

(IV.)   (V.)   (VI.)
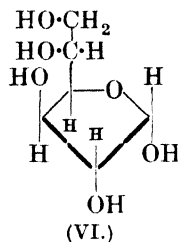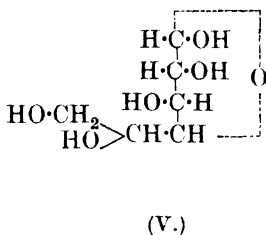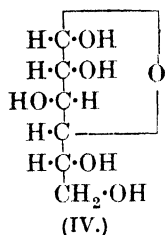
α-Glucofuranose.

The latter two expressions illustrate the spatial proximity of OH groups at C_3 and C_6 and serve to account for the conversion of 3- into 6-monoacetyl glucose derivatives such as the monoacetone compounds, a reaction which involves the wandering of the acyl residue.
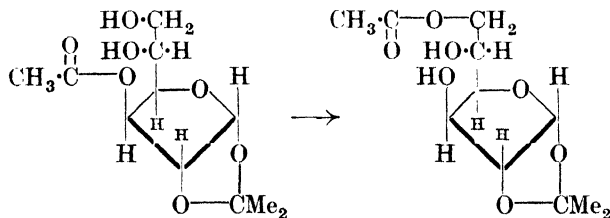
A similar change has been observed with benzoyl derivatives, but in the methyl derivatives this property is not exhibited.

A reinvestigation of the methylated sugars derived from glucose-monoacetone and glucose-diacetone has yielded results confirming the five-atom ring forms of these acetone compounds as opposed to their formulation as four-atom ring sugar complexes. They are to be represented on the basis of the above formulation of α-glucofuranose and, in their formation from ordinary glucose by the agency of mineral acid and acetone, the pyranose structure suffers conversion into the furanose type.[85] Many conflicting data associ-

[84] K. Josephson, *Ber.*, 1929, **62**, [B], 317, 1913; *A.*, 428, 1278; *Annalen*, 1929, **472**, 217; *A.*, 1044; *Svensk Kem. Tidskr.*, 1929, **41**, 99; *A.*, 912.

[85] C. G. Anderson, W. Charlton, and W. N. Haworth, *J.*, 1929, 1329; *A.*, 1044; C. G. Anderson, W. Charlton, W. N. Haworth, and V. S. Nicholson, *ibid.*, p. 1337; *A.*, 1044.

ated with their methyl derivatives in comparison with those of α-fructose-diacetone are removed. In the above and earlier papers the possible existence of a second form of glucose-diacetone was foreshadowed and the formula advanced. A compound which conforms to this isomeride has now been isolated, but, unfortunately, it is a liquid. A number of its transformation products have been investigated [86] and of interest is the crystalline sugar designated 5-methylglucose, which has an unexpectedly high specific rotation for a glucofuranose. The authors' evidence for the orientation of the methyl residue is not yet convincing.

Meanwhile the isolation of glucose-acetone carbonate (VII) and its transformation into simple crystalline glucofuranose (or γ-glucose) derivatives may be considered to have placed the chemistry of γ-sugars on a new basis. The new products which have been isolated [87] are the glucofuranose carbonate (VIII) and its crystalline anilide and osazone, along with the crystalline isomeric forms of α- and β-ethylglucofuranoside (γ-ethylglucoside) (IX and X).
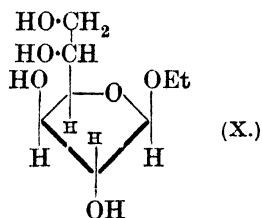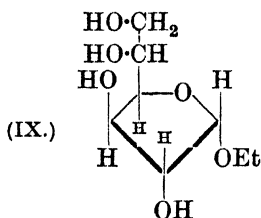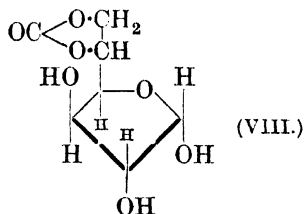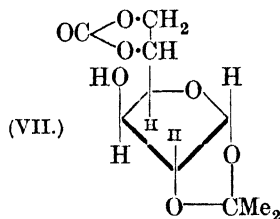
The last two glucosides possess the constitution formerly applied by Fischer to the normal alkylglucosides, and the product (VIII) is the first authentic crystalline derivative of γ-glucose having a free reducing group.

The relationship between sugars of the furanose and the pyranose type is signified by the synthesis from l-trimethyl arabofuranose of the two lactones related to gluco- and manno-pyranose. This is effected by ascent of the series,[88] potassium cyanide and methyl

[86] H. Ohle and L. von Vargha, Ber., 1929, 62, [B], 2425, 2435; A., 1278, 1279.

[87] W. N. Haworth and C. R. Porter, J., 1929, 2796.

[88] W. N. Haworth and S. Peat, ibid., p. 350; A., 425.

chloroformate being used for the preliminary formation of the nitrile, followed by hydrolysis to the acid and lactone. The feature of this synthesis is that the C_4 position is the only point for the attachment of the new six-atom ring when the synthesis is completed and this now becomes C_5 in the *l*-lactones of mannose and glucose which are isolated.
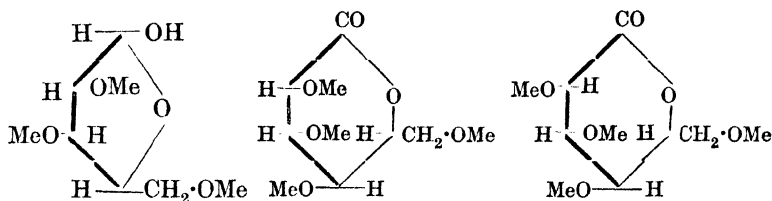
Supplementary evidence to that previously adduced for the occurrence of two types of sugar ring is provided by the correlation of a number of the methylated lactones which have already been serviceable in the elucidation of sugar constitutions. For instance, the five-atom ring lactones derived from gluco- and manno-furanose derivatives are interconvertible by epimerisation in aqueous pyridine; similarly also the methylated lactones from xylo- and lyxo-furanoses. Among six-atom ring forms, the methylated lactones from tetramethyl gluco- and manno-pyranose are interconvertible and so also are the lactones from trimethyl xylo- and lyxo-pyranose. These observations [89] strengthen the constitutional proofs of the various ring structures which have been investigated, and at the same time provide alternative methods for the isolation of a desired lactone.

The development of a novel form of stereoisomerism in the sugar group is made evident by the conclusion that there exist three varieties of triacetyl methylrhamnoside which have an identical structure. Existing theory accounts for only two such forms, α and β, and the third variety is characterised by its possession of exceptional properties. The three acetyl residues are eliminated smoothly and normally from triacetyl α- and β-methylrhamnosides (pyranosides), but the third form loses only two acetyl groups by hydrolysis with alkali. The recalcitrant acetyl group is found to be situated at C_2 in the chain, that is, adjoining the β-methyl residue of the rhamnoside. This anomaly, which extends also to the tetra-acetyl methylmannosides, is interpreted [90] as furnishing evidence of the interlocking of the groups at C_1, C_2, and C_3; and as a working hypothesis it is suggested that this form of the stabilised monoacetyl

[89] W. N. Haworth and C. W. Long, *J.*, 1929, 345; *A.*, 426.

[90] W. N. Haworth, E. L. Hirst, and E. J. Miller, *ibid.*, p. 2469.

β-methylrhamnoside is due to the congestion of the addenda and to a stabilised phase of a non-planar ring.
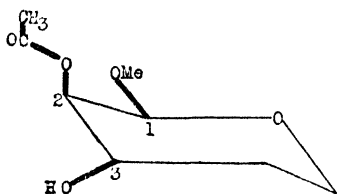
A   B
Unobstructed form.   Interlocked form.
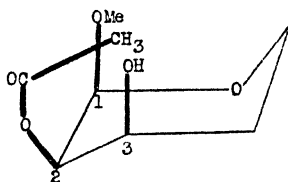
An extension of these experiments may lead to interesting inform- ation on the existence of strainless ring forms of various types.

The oxygen of the C:O group of the acetyl residue may (altern- atively to the CH_3 group) be considered to be enclosed by the OMe and OH groups at C_1 and C_3, and this conception may more easily account for the resistance to hydrolysis of the acetyl group at C_2.

A new classification of the methyl pentoses is rendered possible by the discovery that chinovose, the sugar residue in chinovin, is identical with *iso*rhamnose.[91] Reduction of chinovose yields a sugar alcohol, the benzylidene derivative of which is the same as that prepared by a similar procedure from *iso*rhamnose. A synonym of *iso*rhamnose is *iso*rhodeose, but it is proposed to alter the nomen- clature of the methyl pentoses according to the plan of Votoček and to name them from the hexoses to which they are related. Thus *iso*rhamnose (*iso*rhodeose) will be known as *d*-glucomethylose. Rhamnose and fucose are, however, so commonly known that it is desirable to retain their names rather than to hide them under the new nomenclature as mannomethylose and galactomethylose. On the other hand, new methyl pentoses have been isolated, among which are gulomethylose, talomethylose, and altromethylose, and it is preferable to adopt a systematic terminology which has reference to the parent hexose. *d*-Glucomethylose (*iso*rhamnose), along with altromethylose, has been prepared by the reduction of a new unsaturated compound derived from galactose-diacetone—modified by the introduction of an ethylene group connecting C_5 and C_6. Attachment of hydrogen at these positions in the unsaturated galactoseen furnishes both of these methyloses.

Synthetic Glucosides.—Synthetic methods leading to the formation of α-glucosides are of importance, since only the formation of β-glucosides can be effected with facility by a procedure which is

91 E. Votoček and F. Rác, *J. Czech. Chem. Comm.*, 1929, **4**, 239; *A.*, 682; K. Freudenberg and K. Raschig, *Ber.*, 1929 **62**, [*B*], 373; *A.*, 427.

well recognised. The conditions under which α-glucosides may be prepared have received careful investigation. With the employment to this end of the two reagents, 2-trichloroacetyl-3 : 4 : 6-triacetyl β-glucosidyl chloride and 3 : 4 : 6-triacetyl β-glucosidyl chloride, a yield of 80% or more of α-glucosides has been achieved.[92] These methods may find an application in the synthesis of naturally occurring hexosides, and especially is it to be hoped that methods will soon be available which will lead to the formation of α-galactosides. Meanwhile an extension of the technique in the preparation of β-galactosides is provided by the synthesis of derivatives containing quinol, menthol, and borneol residues.[93]

Alizarin-β-glucosides have been prepared containing (a) one glucose residue, (b) a gentiobiose residue, (c) a cellobiose residue; these are severally well-defined crystalline compounds.[94] Neither (b) nor (c) appears to be identical with ruberythric acid, the synthesis of which has been the objective in the preparation of these glucosides.

The rates of hydrolysis of α-methylglucoside, tetramethyl α-methylglucoside, and trehalose have been determined polarimetrically. The critical increments provided by these results [95] are regarded as more trustworthy than those of velocity coefficients, since the latter ratios vary with the temperature at which hydrolysis is effected. Figures are computed which furnish a measure of the stability of the above compounds, and these are of real utility. An explanation of the ease of hydrolysis of sucrose is discussed, and the author advances evidence in support of the hypothesis that the process of the mutarotation of sugars does not involve a rupture of the oxide ring as is commonly supposed.

Disaccharides.—A new and abundant source of that interesting rare sugar, turanose, has been discovered [96] and its physical constants redetermined. It is probable that this disaccharide will now receive the careful study which its importance demands, and that a new constitutional study will be undertaken. The structure already allocated suggests that turanose may conceivably give the same osazone as gentiobiose, which has not been shown to be the case. The new method for the isolation of gentianose [97] which is reputed to furnish a yield of 24% is of importance inasmuch as this trisaccharide is the chief source of gentiobiose. The latter has

[92] W. J. Hickinbottom, *J.*, 1929, 1676; *A.*, 1167.

[93] A. Robertson, *ibid.*, p. 1820; *A.*, 1167.

[94] G. Zemplén and A. Müller, *Ber.*, 1929, **62**, [*B*], 2107; *A.*, 1281.

[95] A. E. Moelwyn-Hughes, *Trans. Faraday Soc.*, 1929, **25**, 81; *A.*, 405.

[96] C. S. Hudson and E. Pacsu, *Science*, 1929, **69**, 278; *A.*, 1045.

[97] M. Bridel and M. Desmarest, *J. Pharm. Chim.*, 1929, [viii], **9**, 465; *A.*, 856.

hitherto not been obtainable in other than meagre yields from gentian root, although its value for the purpose of synthetic work in the natural glucoside series is apparent.

Useful processes for the isolation of α-alkylbiosides have been recorded.[98] For instance, cellobiose octa-acetate is transformed into α-ethylcellobioside acetate by sublimed ferric chloride dissolved in ethyl alcohol, and the same procedure serves for the preparation of the maltoside from maltose octa-acetate. An alternative method involves the initial formation of acetobromocellobiose.

The introduction of triphenylmethyl residues into a series of di- and tri-saccharides has furnished the interesting generalisation that one such residue enters each primary alcohol grouping. The number of such residues introduced into maltose, sucrose, and raffinose is respectively two, three, and three, in agreement with the requirements for these sugars on the basis of their recently established structural formulæ.[99]

The series of fluoro-, chloro-, and bromo-melibiose hepta-acetates has been isolated,[1] and their physical constants, now made available, are compared with those of the corresponding maltose derivatives, and a regular relationship between these two bioses is established. The author utilises *trans*-strainless models for the hexose units and, although unaware that similar models have been suggested by other workers, has succeeded in tracing certain contrasts in the molecular conformation of α-bioses and β-bioses. This confirms the recognition of the α-configuration of melibiose at the biose junction, a conclusion which was reported in previous years.[2] Suggestive ideas bearing on the conformation of cellobiose and cellulose are made and these receive support from the X-ray diffraction spectra. This preliminary work should lead to further results of considerable interest.

In an attempt to repeat the synthesis of sucrose communicated last year by Pictet and Vogel, other authors [3] have not succeeded in isolating the sugar or its octa-acetate. Pictet and his collaborator have now published [4] fuller details of their work, but similar experiments, in which materials of different but authentic origin have been employed, have led to the isolation of a crystalline *iso*sucrose which is not identical with sucrose.[5] These results mean

    [98] G. Zemplén, *Ber.*, 1929, **62**, [*B*], 985, 990; *A.*, 683.

    [99] K. Josephson, *Annalen*, 1929, **472**, 230; *A.*, 1045.

    [1] D. H. Brauns, *J. Amer. Chem. Soc.*, 1929, **51**, 1820; *A.*, 913.

    [2] *Ann. Reports*, 1927, **24**, 78; 1928, **25**, 104.

    [3] G. Zemplén and A. Gereces, *Ber.*, 1929, **62**, [*B*], 984; *A.*, 683.

    [4] *Ibid.*, p. 1418.

    [5] (Sir) J. C. Irvine, J. W. H. Oldham, and A. F. Skinner, *J. Amer. Chem. Soc.*, 1929, **51**, 1279; *A.*, 683.

that the Pictet–Vogel synthesis can only be accepted with reserve until their results can be imitated by other experimenters.

Polysaccharides.

Inulin.—A review of the literature discloses the existence of a lengthy series of products, based on fructose anhydride, ranging from the simplest member to inulin itself.[6] These products, isolated from different sources, have been regarded as intermediate stages in the polymerisation of the fructose unit to the most complex stage, and in the process of purifying inulin from water the less complex varieties may be separated by reason of their greater solubility. Two of the simpler members of the series have been identified [7] as sinistrin-A, $(C_6H_{10}O_5)_2$, and sinistrin-B, $(C_6H_{10}O_5)_4$. The former has been converted by methylation with methyl sulphate into a compound closely resembling methyl inulin and yielding $3:4:6$-trimethyl fructofuranose on hydrolysis as does trimethyl inulin itself. Conversely it would appear that under a variety of conditions inulin is transformable into simpler complexes.

It has previously been reported that the molecular weight of inulin in liquid ammonia is in agreement with the formula $(C_6H_{10}O_5)_2$, and the same molecular weight has now been determined for inulin dissolved in molten acetamide.[8] The isolation of the polymerised product from the latter mixture is said to yield an inulan which is freely soluble in water and has the composition $(C_6H_{10}O_5)_2$. When preserved, it gradually becomes as insoluble in cold water as inulin, from which it can no longer be easily distinguished. Facts of a similar nature were commented on in the last Report, where it was stated " whether this diminution corresponds to dissociation or decomposition is a problem remaining for future decision." This comment has been misinterpreted by H. Pringsheim as being a criticism of the facts which have been reported.

The synthetic formation of a fructose anhydride is recorded as proceeding from the condensation of fructose with acetone in an acid medium.[9] The product passes into hexamethyl difructose anhydride on methylation and gives rise on hydrolysis to the same trimethyl fructofuranose as obtained by Haworth and Learner from trimethyl inulin. The isolation of an anhydro-fructose of different

[6] H. H. Schlubach and H. Elsner, *Ber.*, 1929, **62**, [*B*], 1493; *A.*, 915; A. C. Thaysen, W. E. Bakes, and B. M. Green, *Biochem. J.*, 1929, **23**, 444; *A.*, 856.

[7] H. H. Schlubach and W. Flörsheim, *Ber.*, 1929, **62**, [*B*], 1491; *A.*, 914.

[8] H. Pringsheim, J. Reilly, and P. P. Donovan, *ibid.*, p. 2378; *A.*, 1282.

[9] H. H. Schlubach and H. Elsner, *Ber.*, 1928, **61**, [*B*], 2358; *A.*, 51.

optical sign is, however, reported [10] as obtainable from inulin, and this again yields a hexamethyl difructose anhydride differing somewhat in physical constants from that described above. It is suggested that inulin contains anhydro-fructose residues of different types in the ratio of 4 : 1. This conclusion seems to be balanced by the observation that glucose may occur as a product of hydrolysis of inulin, and the isolation of traces of this hexose as the penta-acetyl glucose is recorded.[11] It is recognised that this occurrence of glucose may be traceable to a Lobry de Bruyn transformation of fructose.

The fundamental point of view from which all these observations may be considered is that inulin undergoes change with remarkable readiness to give substances of lower molecular weight, and that caution must be exercised in endeavours to reach a conclusion on the molecular complexity of this polysaccharide.[12] The essential mode of linking which occurs in inulin has already been determined and it is seen that the mutual union of adjoining residues of the fructose units must occur through the groups at C_1 and C_2.

This being so, inulin may be regarded merely as a substituted variety of polymerised ethylene oxide. The latter, as has long been known, is readily transformed into polymeric forms of the type $^-O \cdot CH_2 \cdot CH_2 \cdot O \cdot CH_2 \cdot CH_2^-$, etc. In place of pairs of methylene groups separated by oxygen links, the inulin residue is substituted at one of these positions by groups which form a fructofuranose ring, represented by Ⓒ in the expression $^-O \cdot CH_2 \cdot Ⓒ \cdot O \cdot CH \cdot_2 Ⓒ^-$. It must be conceded that, if the polymeric forms of ethylene oxide are constituted on the principle of the exercise of ordinary covalency bonds between adjoining units, as is believed by Staudinger (see following section on polymerisation), then there is no reason to deny the application of a similar principle for the linking of adjoining units in inulin. It is self-evident that the completed molecule of a polymeric form of ethylene oxide is represented by a cyclic structure of the type

$$O \cdot CH_2 \cdot CH_2 \cdot [O \cdot CH_2 \cdot CH_2]_x \cdot O \cdot CH_2 - CH_2$$
$$CH_2 \cdot CH_2 \cdot O \cdot [CH_2 \cdot CH_2 \cdot O]_x \cdot CH_2 \cdot CH_2 \cdot O$$
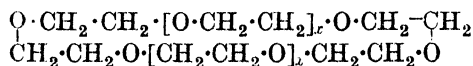
In this the chains may be considered to lie fairly close together in space and to form a kind of flattened loop. Precisely this type of

[10] R. F. Jackson and S. M. Goergen, *Bur. Stand. J. Res.*, 1929, **3**, 27; *A.*, 1280; J. C. Irvine and J. W. Stevenson, *J. Amer. Chem. Soc.*, 1929, **51**, 2197; *A.*, 1046.

[11] H. H. Schlubach and H. Elsner, *Ber.*, 1929, **62**, [B], 1493; *A.*, 915; A. C. Thaysen, W. E. Bakes, and B. M. Green, *Biochem. J.*, 1929, **23**, 444; *A.*, 856.

[12] H. D. K. Drew and W. N. Haworth, *J.*, 1928, 2690; *A.*, 1928, 1360.

structure can be advanced for inulin, and it will be seen that, by adopting this hypothesis, the fructofuranose rings will occur side by side in pairs and in a plane vertical to that of the ethylene oxide chain. The scission of the oxygen links would then be expected to lead to groups of $(C_6H_{10}O_5)_n$, where n is even and has ordinarily the limiting value 2.

$$O \cdot \overset{|}{\textcircled{c}} \cdot CH_2 \cdot [O \overset{|}{-} \overset{|}{\textcircled{c}} \overset{|}{-} CH_2]_x \cdot O \overset{|}{-} \overset{(a)}{\overset{|}{\textcircled{c}}} \overset{|}{-} CH_2$$

$$\overset{|}{C}H_2 \cdot \overset{|}{\textcircled{c}} \cdot O \cdot [CH_2 \cdot \overset{|}{\textcircled{c}} \cdot O]_x \cdot CH_2 \cdot \overset{|}{\textcircled{c}} \cdot \overset{|}{O} \quad \longleftarrow (A)$$

$$(b)$$
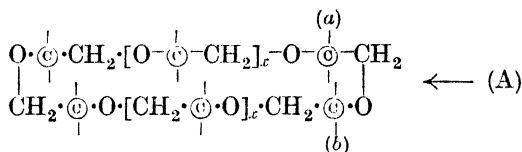
Looked at from (A), the end view of such a model for inulin will show the elevation including the two fructofuranose groups at (a) and (b), and pairs of such units will be perceived at regular intervals throughout the model.
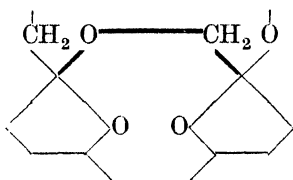
This interpretation is an extension of the work of Haworth and Learner and has not hitherto been advanced quite in this way.

Starch.—The most reasonable hypothesis on which to found a conception of the constitution of starch is that this is composed of conjugated maltose units joined by covalent links.[13] Further support for this view is furnished in a critical paper [14] which discusses the polarimetric values of starch and compares these with the values which would be expected if only α-glucosidic links joined the contiguous pyranose units. The values are such as to suggest that the latter hypothesis is the correct one. The assumption that starch is composed of simple and uniform units of small molecular weight which are " associated " in the complex is considered most improbable. Greater variations occur in the lengths of main valency chains of starch than is the case with cellulose. The kinetics of starch hydrolysis with acids indicates that the action has the same order of magnitude in the initial and subsequent stages and proceeds at nearly the same rate as the hydrolysis of glucosides.

Experiments corresponding to those reported last year are recorded on the formation of triacetyl starches and molecular-

[13] Haworth, " The Constitution of Sugars," London, 1929, p. 84.
[14] K. H. Meyer, H. Hopff, and H. Mark, *Ber.*, 1929, **62**, [*B*], 1103; *A.*, 799.

weight determinations of these products indicate a minimum value of $(C_6H_7O_5Ac_3)_{18}$, but even this value may be due to the occurrence of depolymerisation in the course of acetylation.[15]

Glycogen.—A solution of glycogen in resorcinol does not exhibit the Tyndall effect and is regarded as a molecular and not a colloidal solution : the reverse is the case for aqueous solutions. Preliminary cryoscopic measurements [16] point to a comparatively low molecular weight in the former solvent. Conditions for the complete acetyl- ation and methylation of glycogen have been established and the triacetyl and trimethyl derivatives are described and compared with the corresponding products from starch. Deacetylated glycogen acetate apparently retains the properties of the original poly- saccharide. The trimethyl glycogen yields exclusively 2 : 3 : 6-tri- methyl glucose on hydrolysis and it is emphasised that during methylation of glycogen there is evident no stage of arrest corre- sponding to the introduction of only two methyl residues. It is suggested that glycogen [17] and starch have great similarity in struc- ture and that the former is probably characterised by smaller molecular dimensions.

Cellulose.—Objection is raised to the opinion of Hess that the rotatory power of a solution of cellulose in Schweitzer's reagent is due to a complex formed between copper and every glucose unit of the cellulose complex, and the use made of this view in determining the molecular weight of cellulose is adversely criticised.[18] Equally insecure is the later hypothesis that the structural unit of cellulose is a biosan, since independent attempts to isolate the biosan acetate have shown [19] that this is probably a still highly complex breakdown product of cellulose and is not homogeneous. The isolation of hydrolysis products in apparent agreement with the formulæ $(C_6H_{10}O_5)_3$ and $(C_6H_{10}O_5)_4$ is reported, but it is emphasised that the course of the hydrolysis of cellulose is not in harmony with the conception of a cellulose constitution based on small associated units.[20]

The velocity of hydrolysis of cellulose by hydrochloric acid has been studied both in the absence and in the presence of alkali

[15] Y. Tsuzuki, *Bull. Chem. Soc. Japan*, 1928, **3**, 276; 1929, **4**, 153; *A.*, 175, 1168.

[16] P. Brigl and R. Schinle, *Ber.*, 1929, **62**, [*B*], 99; *A.*, 299; R. O. Herzog and W. Reich, *ibid.*, p. 495; *A.*, 544.

[17] W. N. Haworth, E. L. Hirst, and J. I. Webb, *J.*, 1929, 2479.

[18] D. Macgillavry, *Rec. trav. chim.*, 1929, **48**, 18, 492; *A.*, 262, 763; K. Hess, *ibid.*, p. 489; *A.*, 763.

[19] K. Freudenberg, *Ber.*, 1929, **62**, [*B*], 383; *A.*, 430; J. R. Katz and P. J. P. Samwel, *Annalen*, 1929, **474**, 296; *A.*, 1277.

[20] R. Willstätter and L. Zechmeister, *Ber.*, 1929, **62**, [*B*], 722; *A.*, 544.

chloride.[21]   With dilute acid the ultimate product is hydrocellulose and a linear relationship exists between the rate of hydrolysis and the hydrogen-ion activity of the solution, but a higher reaction velocity is given when the neutral salt is present.   A new determination of the translation lattice of cellulose hydrate [22] has furnished results in agreement with a cell content of eight $C_6H_{10}O_5$ groups as against the recent view of the presence of only four such groups. Interpretations placed upon recent X-ray measurements of cellulose are discussed in the following section on polymerisation.

Xylan.—The constitutional relationship of xylan and cellulose is established by a study [23] of dimethyl xylan, which is now available for the first time as a homogeneous product.   This is formed by two methylation treatments of Esparto xylan and proof is adduced of the presence of methyl residues in the 2- and 3-positions, since a 2 : 3-dimethyl xylose is isolated by hydrolytic cleavage.   It is suggested that the structural formula ascribable to xylan is identical with that given last year to cellulose, except that the side-chain $CH_2 \cdot OH$ groups in the latter are absent from xylan.

Polymerisation.

The slow progress made until recently in the elucidation of the structure of highly polymerised natural substances is to be attributed in large measure to the experimental difficulties which confront the investigator in this field.   The polysaccharides, caoutchouc, and the proteins are difficult to purify, give colloidal solutions, and lack almost all the properties which have hitherto been utilised successfully in structural determinations.

The two main lines of thought concerning the structure of such compounds are differentiated by the views taken of the mechanism involved during polymerisation.   This process is regarded by some workers as depending almost entirely on the forces of auxiliary valency, which may be regarded as being either of a general nature or exerted in the form of definite co-ordinate linkings of the type described by N. V. Sidgwick.[24]   M. Bergmann,[25] for example, holds the view that the polymerised substances are composed of a fundamental unit (Grundkörper), the constituent atoms of which are bound together by co-valent bonds.   The chemical structure is such that the whole of the available valency forces is not employed in the formation of these co-valent linkings.   The unit, therefore,

[21] E. Hunter, *J.*, 1928, 2643; *A.*, 1928, 1334.

[22] K. Weissenberg, *Naturwiss.*, 1929, **17**, 181; *A.*, 493.

[23] H. A. Hampton, W. N. Haworth, and E. L. Hirst, *J.*, 1929, 1739; *A.*, 1167.

[24] " The Electronic Theory of Valency," Oxford (1927).

[25] *Ber.*, 1926, **59**, [*B*], 2973.

possesses strong residual valency, and is capable of associating with other similar units to form an organised whole, the general structure of which is crystalline and may be determined by the method of X-ray analysis. The fundamental unit is not to be regarded as an ordinary substance owing to the fact that it cannot be isolated, any attempt to separate it from solution being foiled by the strong associating power of the unsatisfied auxiliary valency. The latter forces may, however, be so altered in solution that it is possible to obtain values of the molecular weight of the dissolved substance corresponding to that of the fundamental unit. ' Such changes are reversible and the degree of association varies with solvent, temperature, and other external conditions. It follows that the associated solid substances are to be regarded as, in a sense, only apparently highly polymerised.

Arguments in favour of these views are drawn from the results of X-ray analysis. It can be shown by this method that the substances in question are crystalline with small elementary cells containing simple structural units, which are regarded on the above hypothesis as the true molecular units. Further experimental evidence is provided by the marked dependence of the molecular weight of the dissolved substances upon the nature of the solvent, and by the frequency with which values are observed corresponding to those required by the monomeric structural units. Cellulose, for example, appears to dissolve in an ammoniacal copper oxide solution as a glucose anhydride,[26] and a cellobiose anhydride was obtained by M. Bergmann[27] which on isolation had the properties of a highly polymerised substance. Such observations were interpreted by K. Hess in the sense that cellulose is an associated glucose anhydride possessing certain special properties. Some workers have favoured a biose anhydride as the fundamental unit for cellulose.[28] The results of molecular-weight determinations are, however, notoriously difficult to interpret in the case of highly polymerised substances and it appears to the Reporters that little reliance can be placed on the observed values pending a more thorough investigation of the cryoscopic and ebullioscopic behaviour of colloidal solutions.

According to the above views, residual valency plays the most important part in polymerisation, but there are many workers who cannot find in this extension of Werner's ideas a satisfactory explanation of the physical and chemical properties of highly polymerised compounds. They consider, on the contrary, that ordinary co-

[26] *Annalen,* 1923, **435,** 1; *A.,* 1924, i, 142; see also K. Hess, " Die Chemie der Cellulose," Leipzig (1928).

[27] *Annalen,* 1925, **445,** 1; *A.,* 1925, i, 1384.

[28] See P. Karrer, " Die Polymere Kohlenhydrate," Leipzig (1925).

valent linkings are involved in the process of polymerisation and that the polymeride possesses a definite molecular structure containing ordinary co-valent bonds in exactly the same way as the simple organic compounds. The fact that the unit involved in crystal formation is very small offers no particular difficulty,[29] since the results obtained by X-ray analysis can be adequately explained by assuming a regular arrangement of the units linked by co-valent bonds. The views of H. Staudinger, referred to below, and the structures for cellulose suggested by W. N. Haworth[30] and by K. Freudenberg[31] may be cited as representative examples of this point of view.

Certain aspects of the micellar theory of colloids applied to naturally occurring, highly polymerised compounds[32] may be regarded as having points in common with both the above-mentioned hypotheses. A micellar structure has been advanced for cellulose according to which long chains of anhydro-glucose units are joined by covalent links in such a way that cellobiose is formed on hydrolysis. Owing to their molecular size these long chains are said to possess auxiliary valency forces comparable in magnitude with those present in ordinary bonds, and by virtue of these intermolecular forces the chains are held together, giving a three-dimensional array of glucose units which satisfies the conditions demanded by the X-ray observations. The chains of units are not necessarily all of the same length and a bundle of such chains held together by inter-molecular forces forms a micelle. Many of the chemical and physical properties of the substances in question receive a ready interpretation on this basis and, in particular, the baffling problems presented by the viscosity relations of the dissolved substances find a qualitative explanation, arising out of the possible variation in micellar size with change of external conditions. In certain cases it has been possible to calculate the approximate size of the micelle, the dimensions for that present in cellulose being said to be about $20 \times 4 \times 4 \mu\mu$. Ideas similar in their general aspects have been advanced also for certain proteins and for caoutchouc.[33]

The views hitherto referred to have been arrived at principally from a study of natural substances and it has already been pointed

[29] R. O. Herzog, *Naturwiss.*, 1929, **17**, 271; *A.*, 724; compare O. L. Sponsler and W. H. Dore, " Colloid Symposium Monograph," California (1926).

[30] *Helv. Chim. Acta*, 1928, **11**, 534.

[31] *Annalen*, 1928, **461**, 130; *A.*, 1928, 743.

[32] K. H. Meyer and H. Mark, *Ber.*, 1928, **61**, [*B*], 593, 1936; *A.*, 1928, 621, 1228; K. H. Meyer, *Z. angew. Chem.*, 1928, **41**, 935.

[33] K. H. Meyer and H. Mark, *Ber.*, 1928, **61**, [*B*], 1932, 1939; *A.*, 1229, 1252.

out that in many cases, notably with the proteins and caoutchouc, difficulties of isolation and purification form an almost insuperable barrier to progress.   This was realised by Staudinger, who has adopted a different procedure in attempting to elucidate the structure of highly polymerised substances.   He and his collaborators have prepared and studied a large number of comparatively simple polymeric substances and have sought to find models which would serve to explain the structure and behaviour of the more complex natural products.   For example, the insoluble polymeride polyoxymethylene acts in this way as a model for cellulose, and in a similar manner polystyrene serves for caoutchouc, polyvinyl acetate for certain polysaccharides and their derivatives, and the polymerised sodium salt of acrylic acid for colloids of heteropolar character such as the proteins.[34]   The experimental results are described in a long series of publications which have appeared during the course of the past ten years, and the knowledge thus gained has shed an altogether new light on the nature of polymerised substances.

It is obviously impossible to summarise within a few paragraphs the range of investigations conducted by Staudinger and his collaborators, and the polyoxymethylenes will be selected as an example of their general procedure.   Solid polymerised formaldehyde was recognised many years ago [35] as existing in four modifications, differing in physical and chemical properties and designated respectively α-, β-, γ-, and δ-polyoxymethylene.   In 1920 it was suggested [36] that the general principle involved in the structure of these polymerides was the formation of long chains of single formaldehyde molecules in accordance with the scheme

$$\cdots\cdot O—CH_2—O—CH_2—[O—CH_2]_x—O—CH_2\cdots\cdot$$
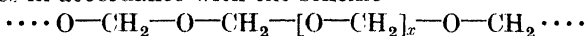
Finally [37] it was recognised that characteristic groups are united to the ends of the chain and that the differences between the various polyoxymethylenes are attributable in large measure to this fact. The α-polyoxymethylenes are polyoxymethylene hydrates with more than 100 formaldehyde molecules in the chain :

$$HO—CH_2—O—[CH_2—O]_x—CH_2—OH.$$

In the γ-polyoxymethylenes the chain is terminated by methyl ether groups, $MeO—CH_2—O—[CH_2—O]_x—CH_2—OMe$, which render the molecules much less reactive and less soluble.   The δ-compounds [38] are dimethyl ethers in which a rearrangement of a certain proportion

[34] H. Staudinger, *Ber.*, 1929, **62**, [*B*], 2893.

[35] F. Auerbach and H. Barschall, *Arb. Kais. Gesundh.-Amt.*, 1907, **27**, 183; *A.*, 1908, i, 131.

[36] H. Staudinger, *Ber.*, 1920, **53**, 1073; *A.*, 1920, i, 517.

[37] H. Staudinger, H. Johner, M. Lüthy, and R. Signer, *Annalen*, 1929, **474**, 155.

[38] H. Staudinger and R. Signer, *ibid.*, p. 232.

of the formaldehyde molecules has taken place, in accordance with the following scheme :

$$\text{MeO—CH}_2\text{—O} \cdots \cdots \cdots \text{CH}_2\text{—O—CH}_2\text{—O—CH}_2\text{—OMe}$$

$$\downarrow \qquad\qquad\qquad\qquad \text{OH}$$

$$\text{MeO—} \cdots \cdots \cdots \text{CH}_2\text{—O—CH}_2\text{—CH—OMe}$$
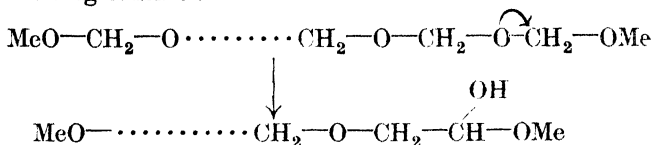
In each series substances corresponding to all grades of polymerisation from $x = 1$ up to $x > 100$ have been prepared and in addition diethyl and dipropyl ethers analogous to the dimethyl derivatives are known, as are also polyoxymethylene diacetates,

$$\text{CH}_3\text{·CO·O—CH}_2\text{—O—[CH}_2\text{—O]}_x\text{—CH}_2\text{—O·CO·CH}_3.$$

$(x = 1 - 50)$.
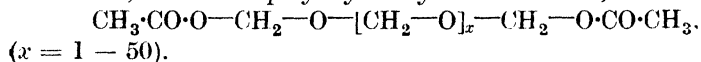
Within any given group the difference in chemical reactivity between closely related " homologues " is generally negligible, and the physical properties change slowly with increase of x, more especially when x is large. A peculiar advantage attends the use of these substances in the study of polymerisation in that the nature of the end group enables a trustworthy estimate of average molecular weight to be made by purely chemical methods, thus avoiding the uncertainties attached to the use of the usual physical methods when high molecular weights are concerned. For example, the methoxyl group in the γ-series may be utilised for this purpose and the length of the chain can be determined by chemical analysis.

It is worthy of remark that γ-polymerides in which the methoxyl content is less than 1% of the molecule differ greatly from the corresponding α-derivatives (dihydrates) in reactivity towards alkali, and Staudinger suggests that here some indication may perhaps be afforded of the way in which minute traces of hormones react in promoting the decomposition of a disproportionately large quantity of a highly polymerised product.

The chemical evidence in the case of the γ-polyoxymethylenes points to a chain containing about 100 formaldehyde residues and having therefore a molecular weight of *ca.* 6000. It is evident, also, that the chains are composed of atoms joined by co-valent links and that auxiliary valencies are not involved in the polymerisation. These highly polymerised substances are not homogeneous in the sense that all the molecules are equal in length and molecular weight. The molecules are, indeed, all built up on the same structural plan, but in any sample of γ-polyoxymethylene some of the component molecules have less and some more than the average number of formaldehyde groups. For such substances the special term " polymereinheitlich " is used.

In the polyoxymethylene series, substances which are homo-

geneous only in this restricted sense are found by X-ray analysis to be crystalline, and interesting questions arise as to the nature of the crystal lattice.   The arrangement of the molecules is such that the long chains are arranged parallel to one another.   This necessarily means that the chemically important end-groups occur at irregular intervals on account of the inequalities in the sizes of the molecules, and these end-groups are therefore not detectable by X-ray methods.[39]

The forces by which the lattice is maintained must be distinguished from those present, for example, in the diamond where all the atoms are bound by principal valencies in every direction.   In the polyoxymethylenes, only in the direction of the length of the chain (i.e., in the molecule itself) are principal valencies involved.   In other directions the forces concerned are inter-molecular and of the order of magnitude of the Van der Waals forces.   The special name, crystallite,[40] is used to describe crystalline materials of this type which consist of unequal large " macro-molecules."   A rough model of the macro-molecule is to be found in a long thin rod.   A bundle of these of different lengths would then form a crystallite, whilst much shorter rods of equal length provide a picture of the polyoxymethylenes of low molecular weight, which consist of molecules containing each the same number of formaldehyde units.

A further question concerns the mechanism by which the crystals of the polyoxymethylenes are built up.   In the lower members of the series, which exist in solution as well as in the solid state, crystal formation follows the normal course, but a different state of affairs is found in the highly polymerised members.   Here the extremely long molecules which make up the crystals cannot exist in solution, but break up into smaller fragments as the result of Brownian movement.   The macro-molecules therefore owe their existence entirely to the fact that when bound together in the crystal their range of movement is restricted by the binding forces.   The formation of crystals containing molecules of very high molecular weight cannot, therefore, take place in the ordinary way by deposition from solution, but must involve the addition of formaldehyde molecules, directly from the gaseous phase or from solution, to polyoxymethylene crystals containing short chains.   This addition is followed by a topochemical reaction which involves the rearrangement of normal valencies and leads to the formation of a substance with a longer chain.   It is important to note that the actual polymerisation takes place in the solid state.

It will be apparent from the above that the arguments previously

[39] H. Staudinger, H. Johner, R. Signer, G. Mie, and J. Hengstenberg, *Z. physikal. Chem.*, 1927, **126**, 425; *A.*, 1927, 647.

[40] H. Staudinger and R. Signer, *Z. Krist.*, 1929, **70**, 193.

advanced in support of the "association" of C_6 or C_{12} units in cellulose now lose much of their significance and in many ways a satisfactory explanation of the properties of cellulose can be obtained by taking polyoxymethylene as a model.[41] Even the characteristic property of fibre formation is imitated by polyoxymethylene. Cellulose, like polyoxymethylene, is crystalline, and possesses a small elementary cell. The low molecular weights observed with some of its derivatives cannot be regarded as valid evidence for the "association" hypothesis, in that the experimental methods involved have not been proved to apply rigidly in the case of colloids, and also because depolymerisation may possibly take place in certain solvents, as actually happens with some polyoxymethylene derivatives. The solubilities of cellulose derivatives favour the view that a macro-molecular structure is present. For example, the acetates tend to be soluble in chloroform and insoluble in water and petroleum, and thus resemble the acetates of the structural unit glucose. This is in agreement with the general rule that those solvents which are good solvating agents for the monomeric substance are capable also of overcoming the inter-molecular forces of the polymeride and producing solvates. Similarly the trimethyl ether of cellulose resembles methylated glucose in being soluble in water.

On this view the derivatives of cellulose are to be regarded as less highly polymerised than cellulose itself, which may be compared with the solid polyoxymethylenes of very long chain. There is a general tendency for solubility to decrease with an increase in the grade of polymerisation and it is for this reason that the extremely long cellulose molecules are insoluble in water and cannot exist as such in solution. In cellulose, as in polyoxymethylene, it is not to be supposed that all the molecules are of equal length, but the substance is one of those to which the term "polymereinheitlich" is applicable. When dissolution takes place and a derivative is formed of lower molecular weight, the extent to which depolymerisation has occurred governs the viscosity of the derivative, gentle reaction conditions giving, for example, highly viscous cellulose acetates. A direct relationship between viscosity and molecular size is obscured by complications arising from a tendency towards the formation of co-ordinate linkings (see below) and it is pointed out in a recent paper [42] that such a relationship certainly cannot hold for aqueous starch solutions.

Some concern may be felt for the nature of the end-groups on this scheme. It is true that in starch and cellulose these groups can represent only a minute fraction of the molecule, owing to the length

[41] H. Staudinger, K. Frey, and R. Signer, *Annalen*, 1929, **474**, 259.
[42] P. Karrer and E. v. Krauss, *Helv. Chim. Acta*, 1929, **12**, 1144.

of the chain.   In starch they may perhaps be accounted for as phosphate ester groupings, but no such masking of the reducing end-groupings can take place in cellulose.   A possible solution of the difficulty is to consider that the lengthy cellulose molecules finally turn round on themselves and become endless chains.[43] It is interesting, therefore, to find a structure of this type suggested in a recent paper on the polyethylene oxides, which are obtained by polymerising ethylene oxide.[44]   The solid polymeride has a ring structure corresponding to the formula

$$O\!\!<\!\!{{CH_2-CH_2-[O-CH_2-CH_2]_x-O-CH_2-CH_2}\atop{CH_2-CH_2-[O-CH_2-CH_2]_x-O-CH_2-CH_2}}\!\!>\!\!O.$$
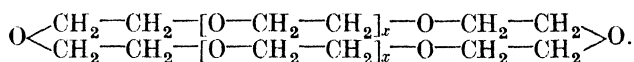
These views may be contrasted with the micellar theory of the colloidal nature of cellulose.   According to Staudinger it is correct to speak of a micelle only if one refers to the whole crystallite of cellulose, which can exist only in the solid state.   The colloidal properties of cellulose derivatives are held to be due not to the fact that the molecules are associated together in micelles, as in certain soap solutions, but to the special properties possessed by very long chains which are equal in size to colloidal particles.   In one direction the chains are colloidal in nature, while being of ordinary molecular magnitude in the other two.

Such conceptions obviously involve new ideas on the structure of organic colloids, and as a model whereby the behaviour of these substances might be further elucidated the polystyrenes were selected.[45]   Here again it has been found that polymerisation of styrene proceeds with the formation of macro-molecules built up according to the following general plan :

$$-\overset{\displaystyle C_6H_5}{CH}-CH_2-[\overset{\displaystyle C_6H_5}{CH}-CH_2]_x-\overset{\displaystyle C_6H_5}{CH}-CH_2-$$
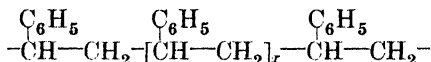
By employing a variety of experimental conditions, polymerides of all grades have been obtained and it has been shown that these polymerides are not micellar in structure, but resemble the polyoxymethylenes in consisting of " polymer-homologues."   Here it is possible, by the use of suitable solvents, to fractionate the products into groups in which the individual molecules differ only slightly in size, and knowledge is thus gained of the variation of physical properties with increasing length of chain.   In particular it appeared

    [43] Compare W. N. Haworth, " The Constitution of Sugars," London (1929).
    [44] H. Staudinger and O. Schweitzer, *Ber.*, 1929, **62**, [*B*], 2395; *A.*, 1268.
    [45] H. Staudinger, M. Brunner, K. Frey, P. Garbsch, R. Signer, and S. Wehrli, *ibid.*, p. 241; *A.*, 305; H. Staudinger, M. Asano, H. F. Bondy, and R. Signer, *Ber.*, 1928, **61**, [*B*], 2575; *A.*, 321; H. Staudinger and H. F. Bondy, *Annalen* 1929, **468**, 1; *A.*, 321.

that the viscosity of solutions of polystyrenes of equal concentration increased as the grade of polymerisation increased, and by making use of these observations it is estimated that some of the products examined had an average molecular weight of more than 100,000. The latter substances must therefore be " macro-molecules " in the sense referred to above and it follows that in certain cases macro-molecular substances are capable of entering into solution. The governing condition is to be found in the nature of the inter-molecular force, which is stronger in the more symmetrical molecules such as the polyoxymethylenes. Hence paraffins of molecular weight of 1000 are insoluble, whereas polystyrenes of molecular weight 100,000 are still readily soluble.

The polystyrenes are therefore similar in structure to the polyoxymethylenes and consist of long chains some 1000 times longer than broad. They are colloidal in one dimension only, and their stability decreases as the length becomes extreme. They are then thermolabile and on heating undergo a " cracking " process with formation of lower homologues. The nature of the end groups present in the higher homologues has not been determined directly, but those of low molecular weight possess ring structures. This fact, considered in conjunction with the work of J. R. Katz [46] on the nature of large rings, renders it very probable that the higher members are also arranged as narrow rings whose sides are close together and parallel.

$$C_6H_5-CH-CH_2-[CH(C_6H_5)-CH_2]_x-CH(C_6H_5)-CH_2$$
$$CH_2-CH(C_6H_5)-[CH_2-CH(C_6H_5)]_x-CH_2-CH-C_6H_5$$
$$(x = 1—500.)$$
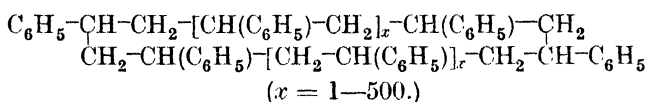
This polymerised hydrocarbon provides a model for caoutchouc and guttapercha, which are constructed on similar lines to the above and whose colloidal properties are dependent not on a micellar structure but on the presence of very long chains, forming macro-molecules. It is suggested that the difference between caoutchouc and guttapercha is one of *cis–trans*-isomerism rendered possible by the presence of the double bond.[47]

Colloids of the types referred to above are designated molecular colloids,[48] since in them the colloidal particle is at the same time the molecule. They are to be distinguished from the micellar colloids, such as the soaps, which are formed by the association of particles of lower molecular weight. Amongst the molecular colloids two divisions may be recognised, it being always remembered that the

[46] *Z. angew. Chem.*, 1929, **42**, 828.

[47] H. Staudinger, *Helv. Chim. Acta*, 1929, **12**, 1183.

[48] For a general account of organic colloids, see H. Staudinger, *Ber.*, 1929, **62**, [*B*], 2893.

dividing line between the sections must be indefinite, since the molecular colloids form a continuous series of gradually increasing molecular weight. When the molecular weight is relatively small (1000—10,000 for polystyrenes), the molecular colloids dissolve without swelling, giving solutions of low viscosity which obey the law of Poiseuille. Such substances do not possess in full the typical colloidal properties and are called " hemi-colloids." On the other hand, substances of greater molecular weight (the labile macro-molecules) show marked swelling with solvents, and give highly viscous solutions, the relative viscosities of which are dependent on pressure and show, therefore, departures from the law of Poiseuille. These are the true colloids, in the sense in which the word was used by Graham, and to distinguish them from the hemi-colloids they are given the name eu-colloids (or macro-molecular colloids).

The homopolar polymerides exemplified by the polystyrenes are comparatively simple cases of natural colloids. Much greater complexity of behaviour is shown by polymerides containing carboxyl, hydroxyl, or other reactive groups (cellulose, starch, etc.). Here the strong dipolar character of the substituent groups may result in the formation of co-ordinate linkings between the molecular chains. The structure is therefore three-dimensional and, when a molecule of this nature is found in solution, still further complications may occur by the formation of co-ordinate linkings between the molecule and the solvent. The most complex of all substances are, however, the heteropolar molecular colloids which are ionised and may at the same time display both marked solvation phenomena and a tendency towards co-ordination. As the model substance for this class, which includes viscose and the protein substances, the polymerides of the sodium salt of acrylic acid [49] have been studied.

It must be emphasised that these organic molecular colloids have no relationship whatever with the so-called colloidal particles of inorganic chemistry (colloidal metals, etc.). The latter are, properly speaking, suspensoids or emulsoids formed by the splitting up of a given substance into small particles. It is possible to obtain a suspensoid by dispersing an organic substance in a solvent in which it is insoluble, but such a suspensoid sol with its roughly spherical particles visible in the ultra-microscope, differs fundamentally from the organic colloids now under consideration. Solutions of the latter are optically empty and the colloidal particles in them are identical with the molecules of the dissolved substance. There is, however, one important inorganic molecular colloid, namely, silicic acid, which is similar in structure to polyacrylic acid.

Both the homopolar and the heteropolar molecular colloids differ

[49] H. Staudinger and E. Urech, *Helv. Chim. Acta*, 1929, **12**, 1107.

from the micellar colloids, the formation of which is due to the inter-molecular forces between comparatively small molecules, and more particularly to the electrical forces situated on ions. An important criterion for distinguishing between micellar colloids and molecular colloids is found in the observation that the former can usually be transformed into derivatives with normal solubilities, whereas the latter invariably give derivatives which dissolve as colloids. Further differences between the two classes are that soluble molecular colloids invariably yield colloidal solutions, whereas association colloids give colloidal solutions in some solvents but not in others, and molecular colloids, apart from " cracking " phenomena, do not alter in size with temperature as does the micelle in an association-colloid.

It is apparent from the foregoing review that Staudinger tends to regard the micellar colloids as of comparatively rare occurrence as compared with molecular colloids. These views, however, are not shared by K. H. Meyer,[50] who maintains that proteins, polysaccharides, and caoutchouc are all built up as micelles formed by the association of long chains of atoms which in turn are linked by co-valent bonds. Even apart from these natural products, he holds that micelle formation is by no means exceptional and cites the behaviour of tannin in water, higher hydrocarbons, substantive dyes, and the lower fatty acids in water.

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W. N. HAWORTH.
E. L. HIRST.

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PART II.—HOMOCYCLIC DIVISION.

THE first discoveries of closed carbon ring-compounds with three-, four-, and five-membered rings were described in the First Pedler Lecture [1] by (the late) W. H. Perkin. This account of his early work reveals the originality and chemical insight displayed by him during those years when he laid the foundation on which Baeyer's " Spannungstheorie " was built.

In accordance with recent practice in these Reports, certain subjects in which considerable progress has been made are nevertheless held over so that they may be more adequately dealt with on a future occasion. This applies particularly to the subject of aromatic substitution, in which important work has been published, especially concerning diphenyl and other dicyclic compounds.

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[50] *Z. angew. Chem.*, 1929, **42**, 76; *A.*, 542.   [1] *J.*, 1929, 1347; *A.*, 904.

Attention may be directed here to a valuable summary of the work of C. K. Ingold and his collaborators in this field [2] and to an interesting theoretical paper by A. Lapworth and R. Robinson.[3]

Dynamic Isomerism and Molecular Change.

(Continued from *Ann. Reports*, 1928, **25**, 118—136.)

The fundamental division of this subject may be made by considering (a) whether an atom or group found to migrate moves within or without the molecule, and (b) if a separation of parts does occur, whether either of these undergoes an internal rearrangement (of atoms or electrons). For instance, the *N*-chloroacetanilide change is only apparently an isomeric change, there being actually no internal rearrangement of the whole or part of the molecule; in prototropy (tautomerism), there is true isomeric change in the organic electromeric ion; in the imino-ether change, the migration is entirely intramolecular.[4] Proved cases of the last type being few, the investigation of a new instance in the triarylbenzenylamidines by A. W. Chapman [5] is of exceptional interest, and not only for this reason but also in that the change involves the novel feature of a reversibly migrating hydrocarbon radical.

The subjects of prototropy, anionotropy, addition to conjugated systems, and migrations of groups will be dealt with in succession.

I. *Prototropy.*—A valuable summary of the theory of prototropic change and its catalysis has appeared from the Leeds laboratory.[6] In the same paper a new case of simple triad tautomerism is described based on the methyleneazomethine system $>CH\cdot N{:}C< \rightleftharpoons >C{:}N\cdot CH<$, the full number of possible triad types constituted from carbon, nitrogen and oxygen atoms being thus realised. Benzylidene-*p*-methoxybenzylamine and *p*-methoxybenzylidene-benzylamine reach the following equilibrium in alcoholic sodium ethoxide solution at 85° : (21·1%) $p\text{-MeO}\cdot C_6H_4\cdot CH_2\cdot N{:}CH\cdot C_6H_5 \rightleftharpoons p\text{-MeO}\cdot C_6H_4\cdot CH{:}N\cdot CH_2\cdot C_6H_5$ (78·9%). The proportions of the isomerides are similar to those in the corresponding three-carbon system.[7]

In a study [8] of the tautomerism of the three α-diketones benzyl-

[2] *Rec. trav. chim.*, 1929, **48**, 797.

[3] *Mem. Manchester Phil. Soc.*, 1927–1928, **72**, 43; *A.*, 546.

[4] J. W. Baker and C. K. Ingold, *J.*, 1929, 423; *A.*, 546.

[5] *Ibid.*, p. 2133; *A.*, 1294.

[6] C. K. Ingold and C. W. Shoppee, *ibid.*, p. 1199; *A.*, 927.

[7] *Idem, ibid.*, p. 447; *A.*, 556; compare *Ann. Reports*, 1928, **25**, 122.

[8] C. Dufraisse and H. Moureu, *Bull. Soc. chim.*, 1927, [iv], **41**, 1607; *A.*, 1928, 180; H. Moureu, *Compt. rend.*, 1928, **186**, 380, 503; 1929, **188**, 504, 1413, 1557; *A.*, 1928, 419; 1929, 449, 883, 929.

methyl-, phenylbenzyl-, and phenyl-*p*-methoxybenzyl-* glyoxals the pure diketone and keto-enol forms have been isolated and in the last two instances the enol was also obtained in *cis*- and *trans*-isomerides, the three forms being

$$Ar·CO·CO·CH_2Ar' \quad Ar·CO·\overset{|}{\underset{|}{C}}·OH \quad \text{and} \quad Ar·CO·\overset{|}{\underset{|}{C}}·OH$$
$$H\overset{}{C}Ar' \qquad\qquad Ar'\overset{}{C}H$$
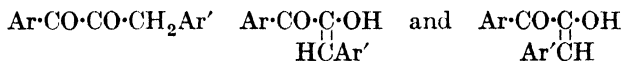
The same equilibrium mixture results from either form of phenyl-benzyl- and benzylmethyl-glyoxals above their melting points and in each case contains 70% of the diketonic form.

The interconversion of the tautomeric forms of ethyl acetoacetate is a unimolecular reversible reaction catalysed by traces of piperidine, ammonia, bromine, pyridine and quinoline, of which the first is about 670 times as effective as the last.[9]

Three-carbon systems. Anions of the type $R\overset{-}{O}$ are arranged in order of diminishing efficiency as catalysts of prototropic change as follows : *iso*propoxide > propoxide > ethoxide > methoxide > hydroxide.[10] A consideration of the inductive effects of the methyl groups at once shows that this is also the order of their diminishing proton-affinity, and is therefore in complete accord with theoretical requirements. The proof of these inequalities comes from a further study of the *cyclo*hexylideneacetone–*cyclo*hexenylacetone system and of the interconversion of the closely related esters ethyl *cyclo*hexylidene- and *cyclo*hexenyl-acetate.[11] There is 57% of the latter (βγ-)ester present at equilibrium, and under similar conditions at 25° the relative speeds of isomeric change in the two systems are indicated by the half-change periods of 9·9 minutes for the ketones and 14·1 hours for the esters.

Analogous ketones of the *cyclo*pentane and *cyclo*heptane series have been synthesised and examined : [12]

$$(CH_2)_n\text{--}C\!:\!CH·COR \rightleftharpoons (CH_2)_n\text{--}C·CH_2·COR$$
$$\diagdown\!\diagup \qquad\qquad \diagdown\!\diagup$$
$$CH_2 \qquad\qquad CH$$
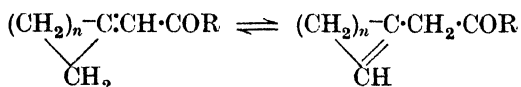
(with $n = 3$ and 5, and R = Me and Et).
The more important data with respect to the equilibration of such

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* Ph·CO·CO·CH$_2$·C$_6$H$_4$·OMe, misnamed phenylanisylglyoxal in both original paper and abstract.

[9] F. O. Rice and J. J. Sullivan, *Trans. Faraday Soc.*, 1928, **24**, 678; *A.*, 35.

[10] G. A. R. Kon and R. P. Linstead, *J.*, 1929, 1269; *A.*, 927.

[11] *Ann. Reports*, 1927, **24**, 110; 1928, **25**, 75.

[12] A. H. Dickins, W. E. Hugh, and G. A. R. Kon, *J.*, 1929, 572; W. E. Hugh, G. A. R. Kon, and T. Mitchell, *ibid.*, p. 1435; *A.*, 560, 1071.

acids and ketones with five-, six-, and seven-carbon rings are collected in the table below.[13]

	Acids (R = OH).		Ketones (R = Me).	
Ring.	%$\alpha\beta$ at equi-librium.	Mobility with 10KOH at 100°. $10(k_1+k_2)$hr.$^{-1}$.	%$\alpha\beta$ at equi-librium.	Mobility with NaOEt at 25°. $10^4(k_1+k_2)$ min.$^{-1}$.
cycloPentane ...	14	22	84	much > 700
cycloHexane ...	12	1·0	43	700
cycloHeptane ...	26	0·66	65	> 3500

The high mobility of cyclopentylideneacetic acid as compared with the cyclohexylidene- and cycloheptylidene-acetic acids is noteworthy, as is also the high mobility and proportion of $\alpha\beta$-ketone at equilibrium in the five-carbon ketone. The authors [12] regard these characteristics as surprising, but an explanation of them and of the high mobility of the corresponding cyclopentylideneacetonitrile (below) may perhaps be found in the strain caused by the presence of the ethylenic linkage in the cyclopentene ring : on the simple tetrahedral theory this will tend to alter the inclination of the single bonds on either side of it to an extent of approximately 31° as compared with the single bond, the angle $\diagdown$C$=$C being 125° in place of $109\frac{1}{2}$° for $\diagdown$C$-$C.

It was to be expected from analogy that the type of tautomerism represented by $>$C$=$C$-$CH$_2$·CN $\rightleftharpoons$ $>$CH$-$C$=$CH·CN would occur, and a few indications of this have been recorded in recent years. For instance, the ready conversion of allyl cyanide into crotononitrile was observed by P. Bruylants in 1922 [14] and by K. von Auwers in 1923,[15] and S. F. Birch and G. A. R. Kon [16] at the same time made a general examination of the reactions of cyclopentenyl- and cyclohexenyl-acetonitriles from this point of view. These and several other nitriles and their $\alpha\beta$-isomerides have now [17] been found to yield equilibrium mixtures under the influence of sodium ethoxide at 25° according to the equation :

$$(CH_2)_n - C:CR·CN \rightleftharpoons (CH_2)_n - C·CHR·CN$$
$$\diagdown CH_2 \qquad \diagup CH$$
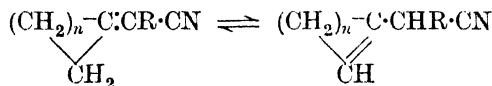
[13] A. A. Goldberg and R. P. Linstead, *J.*, 1928, 2343; *A.*, 1928, 1214; G. A. R. Kon and R. P. Linstead, *loc. cit.*

[14] *Bull. Soc. chim. Belg.*, 1922, **31**, 175; 1924, **33**, 331; *A.*, 1922, i, 817; 1924, i, 1053.

[15] *Ber.*, 1923, **56**, 1172; *A.*, 1923, i, 661.

[16] *J.*, 1923, **123**, 2440.

[17] A. Kandiah and R. P. Linstead, *J.*, 1929, 2139; *A.*, 1294.

The proportions of the isomerides were determined iodometrically and the more important results are given below :

$\beta\gamma$-Nitrile.	%$_0\alpha\beta$ at equilibrium	Mobility. $(k_1+k_2) \cdot 10^4$ min.$^{-1}$.
α-Δ^1-cycloHexenylacetonitrile	95	920
(R = H, n = 4)		
α-cycloHexenylpropionitrile	94	360
(R = CH$_3$, n = 4)		
α-cycloHexenylbutyronitrile	90	74
(R = C$_2$H$_5$, n = 4)		
cycloPentenylacetonitrile	93·5	>1000
(R = H, n = 3)		
β-Methyl-Δ^α-pentenonitrile	99	>1000

The cyano-group has thus a powerful activating effect : the position of equilibrium is altered slightly in the direction to be expected by the introduction of alkyl groups in the α- position. On the other hand, the mobility falls with increased size of these groups. A number of anomalies in the chemistry of unsaturated nitriles are cleared up in this paper, but it may be remarked that in formulating condensation reactions involving substances of this type it should not be forgotten that this is a pentad cyano-imino system, not a simple three-carbon one, and that the nitrogen atom may be directly involved when a sodium salt is produced.[18]

Indirect evidence of an interesting prototropic change has been obtained from the reactions of γ-chloroallyl quaternary ammonium salts discussed below.

II. *Anionotropy.*—Our knowledge of anionotropy continues to develop rapidly, and one important outcome of this is the elucidation of certain problems involved in the addition of halogens to conjugated systems of double bonds,[19] to which reference will presently be made.

An interesting new type of anionotropy has been realised [20] which arises from the influence of an adjacent positive pole as shown in the scheme :

$$CH_2[X] \cdot CH \colon CH \cdot \overset{+}{N}R_3 \; \rightleftharpoons \; CH_2 \colon CH \cdot CH[X] \cdot \overset{+}{N}R_3.$$
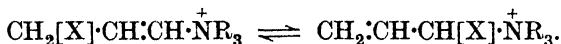
Alcoholic sodium ethoxide readily converts a trialkyl-γ-chloroallyl-ammonium salt into the trialkyl-α-ethoxyallylammonium salt, the constitutions of the initial and the final product being clear from the results of their ozonolysis. This surprising result is satisfactorily interpreted in the following scheme, in which a prototropic change induced by the ethoxide ions is followed by a reaction involving an anionotropic rearrangement :

[18] Compare A. Lapworth and J. A. McRae, *J.*, 1922, **121**, 2741.

[19] *Ann. Reports*, 1928, **25**, 127.

[20] C. K. Ingold and E. Rothstein, *J.*, 1929, 8; *A.*, 300.

$$CHCl{:}CH{\cdot}CH_2{\cdot}\overset{+}{N}R_3\}\overset{-}{X}$$
$$\downarrow OEt'$$

Not isolated.
$$\left\{ \begin{array}{l} CHCl{:}CH{\cdot}\overset{-}{C}H{\cdot}\overset{+}{N}R_3 \quad \underset{\text{prototropic change}}{\xrightleftharpoons{\hspace{2cm}}} \quad \overset{-}{C}HCl{\cdot}CH{:}CH{\cdot}\overset{+}{N}R_3 \\[2ex] \qquad\qquad CH_2Cl{\cdot}CH{:}CH{\cdot}\overset{+}{N}R_3\}\overset{-}{X} \\[2ex] \overset{+}{C}H_2{\cdot}CH{:}CH{\cdot}\overset{+}{N}R_3\}\overset{-}{X} \quad \underset{\text{anionotropic change}}{\xrightleftharpoons{\hspace{2cm}}} \quad CH_2{:}CH{\cdot}\overset{+}{C}H{\cdot}\overset{+}{N}R_3\}\overset{-}{X} \end{array} \right.$$
$$\downarrow OEt'$$
$$CH_2{:}CH{\cdot}CH(OEt){\cdot}\overset{+}{N}R_3\}\overset{-}{X}$$
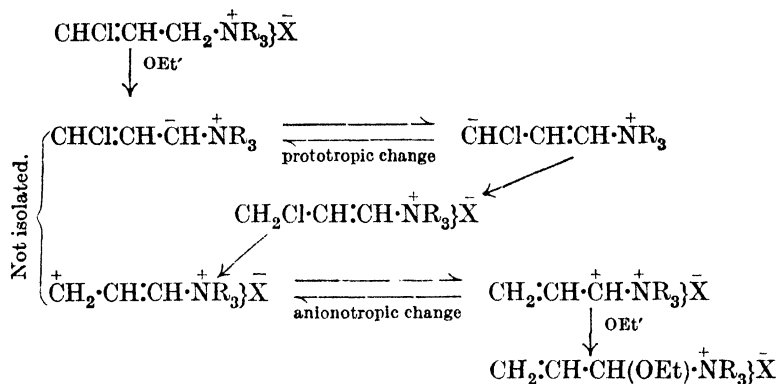
The final product is an ethoxy- and not a chloro-allyl salt because the ethoxide ion has a greater co-ordinating power than the chlorion, and is moreover present in excess.   The ethoxyl group of the final quaternary salt is stable to alkalis, but is hydrolysed by acids.

A comparison [21] of the effects on simple three-carbon anionotropy of adjacent methyl or phenyl groups,

$$\overset{X}{\underset{\curvearrowright}{C}}\quad Me{-}CH{-}CH{=}CH_2 \text{ and}$$

confirms the conclusion reported last year

$$\overset{X}{\underset{\curvearrowright}{C}}\quad Ph{-}CH{-}CH{=}CH_2,$$

that the phenyl group causes the greater activation of the system.

The interconversion of the corresponding ethylpropenyl alcohols and chlorides has been examined by C. Prévost.[22]

Further examples of anionotropic changes in *meso*-substituted anthracene derivatives are recorded by E. de B. Barnett and his collaborators.[23]

III. *Addition to Conjugated Systems.*—A theory of the mechanism of the reduction of unsaturated systems has been put forward by H. Burton and C. K. Ingold [24] which satisfactorily correlates a large number of facts.   It is held that the units added in reduction by metals in aqueous media are not atomic hydrogen but protons and electrons, taken up in successive steps :

$$>C{=}\overset{\frown}{C}{\rightarrow}X \underset{H^{\cdot}}{\rightleftharpoons} >\overset{+}{C}{-}CH{-}X \xrightarrow{2\ominus} >\overset{-}{C}{-}CH{-}X$$
$$\text{(Stage 1.)} \qquad\qquad \text{(Stage 2.)}$$
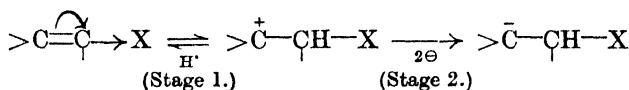
A proton is first added to the molecule which has become polarised

[21] H. Burton, *J.*, 1929, 455; *A.*, 554; *Ann. Reports*, 1928, **25**, 121, 128.

[22] *Compt. rend.*, 1928, **187**, 1052; *A.*, 170.

[23] *J.*, 1929, 1754; *A.*, 1171; *Ber.*, 1929, **62**, [*B*], 423, 1969; *A.*, 448, 1289.

[24] *J.*, 1929, 2022; *A.*, 1270.

at the surface of the metal (stage 1) : the resulting kation next takes up two electrons from the metal (stage 2) : the anion so produced finally combines with a second proton : $>\overset{|}{C}$—$\overset{|}{C}H$—$X \xrightarrow{\overline{H}\cdot}$ $>CH$—$\overset{|}{C}H$—X (stage 3) and the reduction is complete.

If the group X attracts electrons, it will clearly facilitate stage 1 and both inductive and tautomeric effects may assist. In unsaturated acids or ketones the keto-group may perhaps provide an indirect route for the addition of the first proton, in the way suggested by Thiele. At the conclusion of stage 2 the net effect is that negative hydrogen (H^- or H^+, $2\ominus$) has been added. The whole process of reduction is therefore the successive addition of H^- and H^+, whereas addition of bromine is in the order Br^+, Br^-.[25] Consequently the addition of hydrogen to unsaturated systems is related to prototropy in the same way as the addition of bromine is related to anionotropy. The contrast in result is well seen in the fact that $\alpha\delta$-diphenylbutadiene yields a 1 : 2-dibromide but a 1 : 4-reduction product. The observations of R. Kuhn and A. Winterstein [26] that terminally substituted diphenyl-hexatriene, -octatetraene, and -decapentaene all take up hydrogen at the two ends of the long chain are equally in accord with the theory, and much other evidence is presented in Burton and Ingold's paper.

With reference to the addition of bromine to conjugated systems it will be well not to take the partial view that 1 : 2-addition is inherently more direct or probable than 1 : 4-addition. The alternative products are found experimentally to be interconvertible and the theory of anionotropy requires them to be so. It is moreover generally characteristic of the reactivity of tautomeric systems that a reaction which should rationally yield one substance produces its isomeride. To regard this as a two-stage process is an unnecessary assumption. The immediate product in such reactions is frequently found to be " indirect."

The following slight modification of the scheme given in the last Report [27] is free from the particular bias referred to :

$$\text{Reagents} \longrightarrow \begin{cases} \text{ions of 1 : 2-bromide} \rightleftharpoons \text{1 : 2-bromide} \\ \text{ions of 1 : 4-bromide} \rightleftharpoons \text{1 : 4-bromide} \end{cases}$$
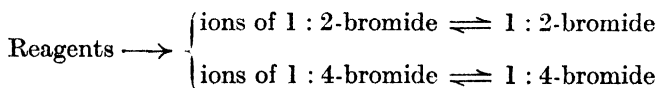
Various circumstances (structural, steric and catalytic) may be expected to share in determining the proportions of the isomerides initially formed.

In a re-examination of the addition of bromine to $\Delta^{1:3}$-*cyclo-*

[25] *Ann. Reports,* 1928, **25**, 131.

[26] *Helv. Chim. Acta,* 1928, **11**, 123; *A.,* 1928, 281.

[27] *Ann. Reports,* 1928, **25**, 132.

hexadiene and *cyclo*pentadiene [28] the results of J. Thiele are substantiated in the latter case, but some 1 : 2-dibromo-Δ^3-*cyclo*pentene is also produced.   The proportion of the 1 : 2- and 1 : 4-products could not be determined quantitatively, but the proof of their structures by oxidation was confirmed.

From *cyclo*hexadiene a new crystalline dibromide is obtained when the bromine is added in chloroform or hexane solution below $-15°$ and the solvent rapidly evaporated at a low temperature.   This substance and a liquid of the same composition which accompanies it are regarded as stereoisomeric 1 : 2-dibromo-Δ^3-*cyclo*hexenes (I). Both are rapidly converted on keeping into the well-known solid 1 : 4-dibromo-Δ^2-*cyclo*hexene (II), which is the chief or sole product

if the bromination is carried out without special precautions.   The authors assert that exclusive 1 : 2-addition has been effected at low temperatures, oxidative degradation of the new substances yielding only succinic acid and no $\alpha\alpha'$-dibromoadipic acid.   But it is also true that no $\alpha\beta$-dibromoadipic acid was found and that the solid 1 : 4-dibromide gave only succinic acid (and no $\alpha\alpha'$-dibromoadipic acid), while analogy with the products from *cyclo*pentadiene (where structures were proved) would suggest that the new liquid isolated is probably a mixture and is likely to contain some of one or both of the possible stereoisomeric 1 : 4-bromides.

The addition of chlorine to α-phenylbutadiene has been found [29] to yield under a variety of conditions only the $\gamma\delta$-dichloride.

IV. *Migrations of Groups.*—In the Report for 1925 [30] an account was given of the conversion of *N*-phenylbenziminophenyl ether into benzoyldiphenylamine by intramolecular change involving the migration of a phenyl group.   A detailed study has since been made of the relative speeds of the change in substituted arylimino-ethers.[31] In the transformation

$$ArO \cdot CPh\text{:}NPh \longrightarrow O\text{:}CPh \cdot NPhAr$$
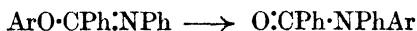
the various groups Ar are arranged in the following order of descend-

[28] E. H. Farmer and W. D. Scott, *J.*, 1929, 172; *A.*, 304.

[29] I. E. Muskat and K. A. Huggins, *J. Amer. Chem. Soc.*, 1929, **51**, 2496; *A.*, 1170.

[30] *Ann. Reports*, 1925, **22**, 114.

[31] A. W. Chapman, *J.*, 1927, 1743; *A.*, 1927, 874.

ing ease of migration : o-nitrophenyl$>2:4:6$-trichlorophenyl$>$ p-acetylphenyl $> 2:4$-dichlorophenyl $> o$-chlorophenyl $> m$-chloro-phenyl$>p$-chlorophenyl and α- and β-naphthyls$>$phenyl and o-anisyl$>m$-anisyl$>p$-anisyl($>$methyl), this order being that of the strengths of the corresponding acids or phenols (Ar·CO_2H and Ar·OH) and therefore of the affinities of these groups for electrons.

On the other hand, with various groups attached (a) to the nitrogen or (b) to the carbon atom of the imino-ether, a phenyl group migrates with a velocity which diminishes in the opposite direction in the above series, for instance, p-anisyl$>$phenyl$>$ chlorophenyls. On these grounds the change may be formulated electronically and the author's view in brief is as follows :
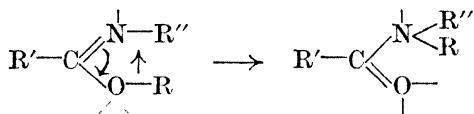
The moving group R carries its binding pair of electrons with it. An intermediate stage is assumed in which R is attached to both the oxygen and the nitrogen atom by singlet linkages. An altern-ative possibility, which accounts better for the influence of variations in R′, is that the initial step is the direct attraction by R of one or both of the lone electrons of the nitrogen atom.

This transformation has found practical use as a method for the synthesis of otherwise inaccessible diphenylamines of determined constitution.[32]

The imino-ether change is quantitative and no reversal can be detected. The corresponding imino-thioether, Ph·S·CPh:NPh, decomposes at the temperatures necessary for such changes, but circumstantial evidence was obtained that a *reversible* conversion to thiobenzoyldiphenylamine, Ph·CS·NPh₂, was also occurring.[33]

It has now been found [5] that the diphenyl-p-tolylbenzenyl-amidines are reversibly interconvertible above 300° :

$$\text{(I.)} \quad PhC{<}^{N\cdot C_7H_7}_{NPh_2} \quad \rightleftharpoons \quad PhC{<}^{NPh\cdot C_7H_7}_{NPh} \quad \text{(II.)}$$
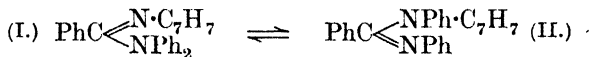
The equilibrium mixture is found by proximate analysis to contain about 65% of (II). The change is seen to be analogous to the tautomerism of the amidines discovered by H. von Pechmann in 1895,[34] and it constitutes the first case of the definitely reversible migration of a hydrocarbon radical.

[32] A. W. Chapman, *J.*, 1929, 569; *A.*, 550; C. S. Gibson and J. D. A. Johnson, *ibid.*, p. 1473; *A.*, 1090.

[33] *Idem, ibid.*, 1926, 2296; *A.*, 1926, 1138.

[34] *Ber.*, 1895, **28**, 869; *A.*, 1895, i, 347.

A new molecular transformation involving the movement of a benzyl group from nitrogen to carbon has been discovered,[35] which would appear to be intramolecular (although it is not, strictly speaking, an *isomeric* change). Phenacylbenzyldimethylammonium bromide is converted readily by aqueous alkali into pure ω-dimethyl-amino-ω-benzylacetophenone :

$$[Ph \cdot CO \cdot CH_2 \cdot \overset{+}{N}Me_2 \cdot CH_2Ph]\overset{-}{O}H \longrightarrow Ph \cdot CO \cdot CH(CH_2Ph) \cdot NMe_2 + H_2O.$$
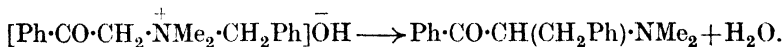
The further investigation of this reaction will be awaited with interest.

The nitroamine–nitroaniline change in 3-bromo-p-tolylnitroamine has been followed quantitatively by a colorimetric method, and earlier results in general confirmed.[36] The reaction is of the first order and is catalysed by various strong acids. Although hydrochloric and nitric acids are equally effective in 50% acetic acid solution, in 98% acetic acid nitric acid has a feeble catalytic effect compared with hydrochloric and other acids. The authors hold that this excludes the possibility of a two-stage process involving hydrolytic liberation of nitric acid which might then nitrate the amine, and conclude that an intramolecular process must play the important part. However, the reaction is not quantitative (as a truly intramolecular change should be), nor is it free from side reactions. The occurrence of extra-nuclear migration of the nitro-group to a foreign aniline nucleus has, moreover, been detected. It is possible that some other explanation may be found for the curious catalytic effects mentioned. If the actual reagent in nitration were nitrous acid or nitroxyl chloride, some such effects might occur.

The claim of B. Flürscheim and E. L. Holmes [37] to have found a case of intramolecular *meta*-migration from the side chain into the nucleus during the nitration of phenylbromocyanonitromethane has been very completely disproved by J. W. Baker and C. K. Ingold.[38] On the other hand, the latter authors regard the production of p-nitrobenzoyl cyanide in the same reaction as due to the *para*-migration of a nitro-group in the decomposition of the original nitromethane, and reactions are discussed which may account for the products observed. In this instance, once again, the fact that no simple quantitative change can be followed makes it wiser to remain sceptical as to whether any intramolecular change is involved.

The movement of various acyl groups from one oxygen atom to

[35] T. S. Stevens, E. M. Creighton, A. B. Gordon, and M. MacNicol, *J.*, 1928, 3193; *A.*, 180.

[36] A. E. Bradfield and K. J. P. Orton, *J.*, 1929, 915; *A.*, 804.

[37] *J.*, 1928, 453; *A.*, 403.   [38] *J.*, 1929, 423; *A.*, 546.

another of polyhydroxyanthraquinones is found to occur only between adjacent hydroxyl groups [39] and may be regarded as involving a cyclic intermediate :

$$\begin{array}{ccc} \diagup\text{OH} & \diagup\text{O}\diagdown\text{C}\diagup\text{OH} & \diagup\text{O·CO·CH}_3 \\ \diagdown\text{O·CO·CH}_3 \longrightarrow & \diagdown\text{O}\diagup\text{}\diagdown\text{CH}_3 \longrightarrow & \diagdown\text{OH} \end{array}$$
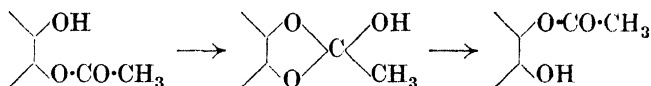
The conversion of phenyl benzyl ether [40] into 4-benzyl- and 2 : 4-dibenzyl-phenols by zinc chloride is largely or entirely an intermolecular process. The same is presumably true of the change of β-naphthyl methyl ketone into its α-isomeride,[41] catalysed particularly by hydrochloric acid.

A definite disproof of the independent existence of an intermediate of the type $Ph·CO·N<$ sometimes postulated to account for the Curtius and Hofmann reactions appears to be provided by the observation [42] that benzoylazide decomposes in presence of triphenylmethyl, yielding only the usual products : $Ph·CO·N_3 \longrightarrow N_2 + PhNCO$. Any such reactive nitrogen compound would be expected to combine to some extent with the triphenylmethyl.

Physical Properties of Benzene Derivatives.

(Continued from *Ann. Reports*, 1926, **23**, 143—149.)

Recent work on X-ray crystal analysis, on direct and indirect examination of spectra in the infra-red region, and on the electrical and magnetic properties of organic substances has provided a definite answer to one of the most important questions of organic chemistry, namely, that of the structure of benzene. The results obtained by each of these three physical methods of investigation support the conclusion that the benzene ring is normally of flat hexagonal shape with the atoms all lying in a single plane.

I. X-*Ray Investigation.*—It should be pointed out in the first place that Sir William Bragg's formulæ for the carbon skeletons of aromatic hydrocarbons,[43] in which the atoms are represented as not all lying in a single plane, were not completely proved, but were adopted as being consistent with the X-ray observations then obtained and with the preservation of the tetrahedral disposition of valencies as in diamond.

A complete solution of the structural problem for hexamethylbenzene has now been obtained by (Mrs.) K. Lonsdale [44] without

[39] A. G. Perkin and C. W. H. Story, *J.*, 1929, 1399; *A.*, 1074.

[40] W. F. Short and M. L. Stewart, *ibid.*, p. 553; *A.*, 552.

[41] L. Chopin, *Bull. Soc. chim.*, 1929, [iv], **45**, 167; *A.*, 561.

[42] G. Powell, *J. Amer. Chem. Soc.*, 1929, **51**, 2436; *A.*, 1176.

[43] *J.*, 1922, **121**, 2783.

[44] *Trans. Faraday Soc.*, 1929, **25**, 356; *A.*, 750.

making any arbitrary assumptions. All twelve carbon atoms of the substance lie in one plane, deviations from it not exceeding 0·1 Å. The ring is a hexagon identical in size with those to be found in graphite. The nuclear carbon atoms are thus of diameter 1·42 $\pm$ 0·03 Å., whereas the side-chain carbon atoms are different, being in fact of the size found in diamond and aliphatic substances (diameter 1·54 Å.). Other dimensions of benzene are : distance from centre to centre of *meta* carbon atoms, 2·46 Å. ; breadth in this same direction, including the two hydrogen atoms, 6·23 Å. ; diameter inclusive of hydrogen atoms in *para*-direction, about 7 Å.

There can be little distortion of the hexagon, yet, as the symmetry is not completely hexagonal, the view is adopted that some distortion must occur. It would appear possible, however, that the disposition of the hydrogen atoms of the methyl groups might provide a sufficient explanation without any distortion of the ring.

The result is of the greatest importance for aromatic chemistry. The unsymmetrical introduction of polar substituents into the ring might conceivably slightly alter the shape of the ring, but it will be well to assume that the flat hexagonal structure with valencies all in one plane is the rule among all aromatic nuclei until evidence is found of deviation from a single plane.

The fate of the fourth valency of the nuclear carbon atoms is left undecided by these results. A formula for naphthalene has also been discussed,[45] which accounts for the X-ray results with this substance, and in which an " anisotropic carbon atom " is present having two pairs of valencies of different type.[46]

Less definite but interesting results are obtained from the diffraction of X-rays by liquids. The haloes produced are regarded [47] as due to structure. It is possible by this means to distinguish between isomerides,[48] to detect the presence of long, flat, or doubled molecules, and to calculate approximate molecular dimensions.[49] The mean distance between molecules of paraffins with five to eight carbon atoms and also of very long-chain compounds is about 4·9 Å. perpendicular to their length. The dimensions found in two perpendicular directions are 6·2 and 3·2 Å. for benzene and 6·4 and 4·6 Å. for *cyclo*hexane. The diameter of menthone is found as

[45] (Mrs.) K. Lonsdale, *Proc. Leeds Phil. Soc.*, 1929, **1**, 346; *A.*, 307.

[46] See ref. 56.

[47] K. S. Krishnan and S. R. Rao, *Indian J. Physics*, 1929, **4**, 39; *A.*, 1129.

[48] C. M. Sogani, *ibid.*, 1927, **1**, 357; **2**, 97; *A.*, 1927, 924, 1129.

[49] V. I. Vaidyanathan, *ibid.*, 1929, **3**, 371, 391; *A.*, 746, 751; P. Krishnamurti, *ibid.*, pp. 331, 507; *A.*, 751, 989; G. W. Stewart, *Physical Rev.*, 1929, [ii], **33**, 889; *A.*, 985; J. R. Katz and J. Selman, *Z. Physik*, 1928, **46**, 393; *A.*, 1928, 222.

5·35 Å., that of cadinene about 7 Å. Somewhat similar information is obtainable by measurements of viscosity in vapours.[50]

II. *Infra-red Absorption and Raman Spectra.*—A valuable general review of the significance of molecular spectra has appeared.[51] The investigation of structure by means of the infra-red absorption is becoming of increasing importance and the recent discovery of the " Raman effect " has provided a new and rapid method of attack in the same direction.[52]

When a substance is illuminated with monochromatic light, the spectrum of the scattered light contains lines or bands which are evidence of characteristic frequencies of the molecule and correspond with infra-red lines. The infra-red band found at a wave-length of about 3·4 μ in the spectra of organic substances and regarded at first as due to CH_2 and CH_3 groups is now attributed to the C·H linkage.[53] This band, as confirmed by the Raman method, is at 3·4 μ in paraffin hydrocarbons and at 3·25 μ in benzene,[54] values nearer the latter figure being found for ethylene and tetrachloroethane. The Raman spectrum of toluene reveals the two lines side by side with wavelengths of 3·43 and 3·28 μ respectively. A detailed study of the Raman spectra of hydrocarbons by A. S. Ganesan and S. Venkateswaran [55] confirms the difference in frequency of the C·H bonds in benzene and *cyclo*hexane.

The values undoubtedly indicate that the C·H bond in benzene and in compounds such as chloroform is stronger than that in paraffins or in *cyclo*hexane. The conclusion is also reached that there may be two different kinds of C·H bond originating at one carbon atom, which conception is in agreement with a similar one derived from X-ray data for hexachloroethane.[56]

III. *Electrical and Magnetic Properties.*—(a) *Optical, electrical and magnetic anisotropy.* In an analysis of the physical peculiarities of aromatic compounds, (Sir) C. V. Raman and S. Bhagavantam [57] emphasise the fact that these substances are characterised by a high

[50] T. M. Lowry and A. G. Nasini, *Proc. Roy. Soc.*, 1929, [*A*], **123**, 686, 692, 704; *A.*, 637.

[51] W. E. Garner and J. E. Lennard-Jones, *Trans. Faraday Soc.*, 1929, **25**, 611; and succeeding papers.

[52] (Sir) C. V. Raman and K. S. Krishnan, *Indian J. Physics*, 1928, **2**, 399; *A.*, 1928, 1075.

[53] G. B. Bonino, *Gazzetta*, 1923, **53**, 555; *A.*, 1923, ii, 711; J. W. Ellis, *Physical Rev.*, 1924, **23**, 48; *A.*, 1924, ii, 219.

[54] P. Pringsheim and B. Rosen, *Z. Physik*, 1928, **50**, 741; *A.*, 1928, 1307; G. B. Bonino, *ibid.*, 1929, **54**, 803; *A.*, 740.

[55] *Indian J. Physics*, 1929, **4**, 195; *A.*, 1215.

[56] (Mrs.) K. Lonsdale, *Phil. Mag.*, 1928, [vii], **6**, 433; *A.*, 1928, 1079.

[57] *Indian J. Physics*, 1929, **4**, 57; *A.*, 1126.

optical, electrical, and magnetic anisotropy both in the crystalline and in the fluid state.

Experiments on the molecular scattering of light in liquids [58] and the double refraction of crystals show the optical anisotropy of aromatic compounds to be generally large as compared with that of aliphatic compounds. The difference is very inadequately revealed by the values of molecular refractivity, because this property represents an average in all directions in space. An even greater difference is shown in electrical and magnetic anisotropy by aromatic and aliphatic compounds, as indicated in the liquid state by the Kerr and the Cotton–Mouton constants, and also in the crystalline state.[59] cycloHexane behaves as an aliphatic substance in these respects. These physical differences are closely paralleled in the properties of graphite and diamond, which may be regarded as of the aromatic and the aliphatic type respectively.

This paper [57] also contains a discussion of the molecular mechanism responsible for these properties and for light absorption, attention being directed to the conceptions of S. Dutt.[60]

(b) *Dipole moments of organic substances* (continued from *Ann. Reports*, 1926, **23**, 147—149). The publication of an authoritative work by P. Debye on the subject of molecular polarisation will be generally welcomed.[61] Research in this field is proceeding so rapidly that the literature dealing with this property of organic substances is already voluminous.

Values of the dipole moments of organic substances are tabulated below, including some aliphatic compounds, as these are necessary for the discussion of the additive nature of the moment. All available data have been considered in compiling this table, and in some cases the mean of more than one independent datum is given, but all important references are added. Most of the values have an uncertainty of about 0·1, although some are certainly more precise.

Dipole Moments. Unit $= 10^{-18}$ *E.S.U.*

(1) Hydrocarbons and Monosubstituted Compounds.

	$\mu.$		$\mu.$
Hydrocarbons :		Alkyl halides : [63, 66]	
Olefins [62, 63]	0·5	Chlorides	2·1
Toluene [64]	0·5	Bromides	1·9

[58] K. S. Krishnan, *Phil. Mag.*, 1925, [vi], **50**, 697; *A.*, 1925, ii, 1030.

[59] M. Ramanadham, *Indian J. Physics*, 1929, **4**, 109; *A.*, 122; S. Bhagavantam, *Proc. Roy. Soc.*, 1929, [*A*], **124**, 545; *A.*, 982.

[60] *J.*, 1926, 1171; *A.*, 1926, 830.

[61] " Polar Molecules " (Chemical Catalog Co., 1929).

[62] C. P. Smyth and C. T. Zahn, *J. Amer. Chem. Soc.*, 1925, **47**, 2501.

[63] K. Höjendahl, *Physikal. Z.*, 1929, **30**, 391; *A.*, 980.

[64] J. W. Williams, *ibid.*, 1928, **29**, 174, 683; *A.*, 1928, 578, 1180.

	μ		μ
Alcohols [64, 65, 66]	1·68	Iodides	1·85
Phenol [64]	1·70	Aryl halides : [63, 64, 66, 67, 70, 71]	
Ethers : [63, 64, 67, 68]		Fluorobenzene	1·38
Aliphatic	1·2	Chlorobenzene	1·55
Anisole	1·2	Bromobenzene	1·5
Diphenyl ether [67]	1·0	Iodobenzene	1·2
Ethylene oxide [68]	1·88	Nitriles : [63, 72]	
Ketones : [63, 64, 69]		Aliphatic	3·4
Aliphatic ; cyclohexanone	2·73	Benzonitrile	3·8
Aldehydes :		Amines : [63, 67, 73]	
Acetaldehyde [63]	2·7	Aliphatic $R \cdot NH_2$ 1·3; R_2NH 1·0;	
		R_3N 0·76	
Benzaldehyde [64]	2·75	Aromatic $Ph \cdot NH_2$ 1·5; Ph_2NH 1·3;	
		$Ph \cdot NMe_2$ 1·4	
Benzoic acid [64]	1·0	Nitro-compounds : [63, 64, 67]	
Esters :		Nitromethane	3·05
Aliphatic [64]	1·7	Nitrobenzene	3·90
Methyl benzoate [67]	1·8		

(2) Disubstituted Benzenes.[63, 64, 66, 67, 70, 71, 74]

		μ.			μ.			μ.			μ.
Me : Me	$\{$	o- 0·5	Cl : Cl	$\{$	o- 2·3	Cl : NO₂	$\{$	o- 4·1	NO₂ : CO₂H		p- 3·5
		m- 0·5			m- 1·55			m- 3·4	NO₂ : NO₂	$\{$	o- 6·0
OH : Me	$\{$	o- 1·4	Br : Br	$\{$	o- 1·7			p- 2·55			m- 3·8
		m- 1·6			m- 1·3	Br : NO₂		p- 2·53			
		p- 1·6	I : I		o- 1·3	NO₂ : OMe	$\{$	o- 4·80	NO₂ : Me	$\{$	o- 3·7
OMe : Me	$\{$	o- 1·0		$\{$	o- 1·73			p- 4·36			m- 4·3
		m- 1·2	Br : I		m- 1·1						p- 4·5
		p- 1·2			p- 0·5	NO₂ : NH₂	$\{$	o- 4·45	CO₂Me : CO₂Me	$\{$	o- 2·8
Cl : Me	$\{$	o- 1·4	Cl : OH	$\{$	o- 1·3			m- 4·72			p- 2·2
		m- 1·6			p- 2·4			p- 7·1	NH₂ : CO₂Me	$\{$	o- 1·0
		p- 1·7				NO₂ : CHO		p- 2·4			m- 2·4
											p- 3·3

Substances found to have negligible moments are : paraffins, benzene, diphenyl, *p*-xylene, *s*-trialkylbenzenes, *p*-dichloro- and dibromo-benzenes, *s*-tribromobenzene. In homologous series the values are generally remarkably constant, with some exceptions in the case of the first member. The effects of temperature are fully discussed by Debye [75] and others.[65, 67, 70, 76]

[65] (Miss) L. Lange, *Z. Physik*, 1925, **33**, 169; C. P. Smyth and W. N. Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312, 3330; S. Mizushima, *Proc. Imp. Acad. Tokyo*, 1929, **5**, 15; *A.*, 380.

[66] P. Gross, *Physikal. Z.*, 1929, **30**, 504; *A.*, 1128.

[67] G. Hedestrand, *Z. physikal. Chem.*, 1929, *B*, **2**, 428.

[68] H. A. Stuart, *Z. Physik*, 1928, **51**, 490.

[69] K. L. Wolf, *Z. physikal. Chem.*, 1929, *B*, **2**, 39; **3**, 128; *A.*, 743.

[70] C. P. Smyth, S. O. Morgan, and J. C. Boyce, *J. Amer. Chem. Soc.*, 1928, **50**, 1536; *A.*, 1928, 815.

[71] P. Walden and O. Werner, *Z. physikal. Chem.*, 1929, *B*, **2**, 10.

[72] J. W. Williams, *ibid.*, 1928, **138**, 75; *A.*, 121; O. Werner, *ibid.*, 1929, *B*, **4**, 371; *A.*, 1217.

[73] A. Weissberger and R. Sängewald, *ibid.*, **5**, 237; *A.*, 1217; A. Weissberger and J. W. Williams, *ibid.*, **3**, 367; *A.*, 866.

[74] C. P. Smyth and S. O. Morgan, *J. Amer. Chem. Soc.*, 1927, **49**, 1030; *A.*, 1927, 611.   [75] *Op. cit.*, pp. 19, 55.

[76] O. Werner, *Z. physikal. Chem.*, 1929, *B*, **4**, 393; *A.*, 1217.

E

The approximately additive nature of dipole moments in the benzene series is now generally admitted, but some divergence of opinion has arisen as to their detailed interpretation. Two classes of compound may be distinguished, (a) those with groups such as OR, OAc, NR_2 absent from the molecule, and (b) those in which one or more of these groups are present.

In the former class, with other polar groups such as CH_3, NO_2, and halogens, vector addition of their moments seems to hold without any large deviation.[63, 64] The compounds of zero moment mentioned above are of this type and these results are evidence that the groups and the ring lie in a single plane. In this connexion, however, the case of s-trinitrobenzene is of interest,[64, 67] as this substance has a real moment of 1·08 units.[77] But it is not necessary to regard this as indicating that the molecule is non-planar : a compound of this substance with benzene (used as solvent) is known, which has recently been given an unsymmetrical formula.[78] Some of this complex is presumably present in solution and may account for the observed moment.

The simple vector addition of dipole moments has been discussed by J. W. Williams,[64] who gives the following series of group values :

NO_2.	CHO.	OH.	Cl.	Br.	OMe.	CO_2H.	CH_3.	NH_2.
$-3\cdot8$	$-2\cdot8$	$-1\cdot7$	$-1\cdot5$	$-1\cdot5$	$-1\cdot2$	$-0\cdot9$	$+0\cdot4$	$+1\cdot5$

The position of the groups OH and NH_2 is criticised by P. Walden and O. Werner,[71] and these are referred to again below. These authors analyse the slight deviations from the additive law for compounds of class (a) and conclude that there is a regular tendency for the moment of an o-disubstituted benzene to be low (actually, to have a smaller negative value than that calculated), which they attribute to the mutual influence of the groups.

Reference should also be made to diphenyl derivatives. Evidence concerning these was mentioned in the last Report,[79] and other results have appeared [80] which give no support to the Kaufler formula.

With the second class of substances (b), having one or more of the groups OH, OR, NH_2, NR_2 and OAc present in the molecule, an important new factor becomes evident.[63, 64, 71] Compounds of apparently symmetrical formulæ give real moments as follows : quinol diethyl ether, 1·7 ; quinol diacetate, 2·2 ; tetramethyl-p-phenylenediamine, 1·23 ; tetramethylbenzidine, 1·25 ; phloro-

[77] P. Debye, op. cit., p. 52.

[78] G. M. Bennett and G. H. Willis, J., 1929, 259; A., 436.

[79] Ann. Reports, 1928, **25**, 116.

[80] E. Bretscher, Helv. Phys. Acta, 1928, **1**, 355; A., 980.

glucinol trimethyl ether, 1·8; dimethyl terephthalate, 2·2 (unit, 10^{-18} E.S.U.). The group of compounds $C(CH_2X)_4$ may also be mentioned : where $X = Cl$, Br or I, the expected zero moment was realised,[81] but when $X = OR$ or OAc this is not the case, penta-erythritol tetra-acetate giving the value $1·9 \times 10^{-18}$ unit.[64] The explanation of these anomalies lies in the fact that the moments of these groups do not operate along the line of their attachment to other atoms. That this must be so follows from the formulæ for the water and ammonia molecules which have been discussed by Debye.[82] An explanation of this kind, which has been used by several workers,[63, 64, 69] immediately accounts for the existence of a real moment in all molecules of class (b) and renders superfluous such conceptions as that of a carbon atom of pyramidal configuration.

The bond from oxygen or nitrogen to the nucleus is presumably fixed in direction, but rotation of the whole group on this line is possible and introduces an uncertainty in calculation. The best plan appears to be to calculate the upper and lower limits to the value of the moment. Thus a calculation on assumptions to be discussed below indicates that in the extreme positions (I) and (II) of rotation in quinol diethyl ether the moment should be

(I.)   Et — O — nucleus — O — Et   (II.)

0·0 and 1·9 units respectively, the observed value being 1·7, but a slight rise of this value with increase of temperature which has been detected [76] was scarcely to be expected.

It is shown by A. Eucken and L. Meyer [83] that it is not justifiable to take the resultant moment of a group OEt as operating along the line O·Et as some authors have done. The molecular moment is regarded as the vector-sum of a number of single moments each in the direction of a separate interatomic bond. For the purpose of summation, however, these may be compounded for any rigid system such as $C·CH_3$. In these calculations the bonds attached to oxygen in an ether are assumed to be inclined at an angle of 110°,[84] and for amines the same angle between valencies seems to be a reasonable supposition.

Component moments deduced by these authors are :

C—C	H—O	C=O	CH_3—C	H—C	C—O	C—Cl
0	1·6	2·3	0·4	0·4	0·7	1·5

[81] L. Ebert, R. Eisenschitz, and H. von Hartel, *Z. physikal. Chem.*, 1928, *B*, **1**, 94; *A.*, 1928, 1308.

[82] *Op. cit.*, pp. 63, 73.   [83] *Physikal. Z.*, 1929, **30**, 397; *A.*, 980.

[84] Compare the second configuration of H_2O; P. Debye, *op. cit.*, p. 73.

Fair agreement is found with the observed values; for instance, the calculated values for phenol, p-chlorophenol and alkyl chlorides are 1·5, 2·3 and 1·9 respectively (Found : 1·6, 2·4, 2·1). The three cresols present a case where rotation will cause variation : values calculated are o- 1·2—1·9, m- 1·2—1·9, p- 1·5 (Found : 1·4, 1·6, 1·6).

The experimental figures for p-nitroanisole and p-nitroaniline are by any method of calculation abnormally large (nitroanisole : calc., 3·3 ; found, 4·36) and the conclusion is inevitable that there is here a considerable mutual influence of the groups.[63]   There appears in fact to be a permanent conjugative displacement of electrons (T effect), causing an enhanced moment, and its magnitude is in the order $N>O>Cl$.   This explains the large separation of OH and NH_2 in the group series of Williams.

The physical evidence reported in this and the preceding sections is consistent in indicating a flat hexagonal ring structure for the benzene molecule and in excluding several of the older formulæ, such as those of Baeyer, Körner, Ladenburg, and Sachse.   The model due to L. Pauling [85] is most in accordance with the facts under consideration [57, 74] and appears to resemble closely the formula of Claus.   Such a formula justifies the scheme given by Ingold [2] to account for the transmission of electrical effects in the nucleus during aromatic substitution, and should remove any objections which may be held to the *para*-bond.   Such a bond cannot admittedly be the ordinary chemical bond between carbon atoms, for the distance is here about twice the normal, but it may safely be assumed that there is an intimate electrical connexion between the p-atoms.

Replacement of Halogens by other Groups.

This subject may be divided into two parts dealing with the reactivity of (a) nuclear and (b) side-chain halogens.

I. *Nuclear Halogen.*—It is one of the most important advantages of the theory of aromatic reactivity originated by Lapworth and Robinson that it supplies a satisfactory explanation of the reactivity of halogen in such substances as p-chloronitrobenzene.   This type of reaction, which essentially involves attack by a negative ion, has not been discussed recently in these Reports.

The fact that other *meta*-directing groups such as SO_3H, CO_2H, CHO and CN are also able to activate nuclear halogens in the o- or p-positions to them was shown by M. Schöpff as far back as 1891,[86] and known instances of such effects are numerous.   Polynitro-chloronaphthalenes have equally displaceable halogen.[87]   The

[85] *J. Amer. Chem. Soc.*, 1926, **48**, 1132; *A.*, 1926, 662.

[86] *Ber.*, 1891, **24**, 3771; *A.*, 1892, 335.

[87] F. Ullmann and W. Bruck, *Ber.*, 1908, **41**, 3932; *A.*, 1909, i, 21; M. Rindl, *J.*, 1913, **103**, 1911.

displacement of activated halogens by a variety of reagents was studied particularly by W. Borsche [88] and by Kenner [89] and the reaction with piperidine has proved valuable in the hands of Turner and his collaborators for deciding questions of orientation, particularly in the diphenyl series : [90] a rapid substitution of the piperidyl radical for halogen is proof that the latter stood in either an *o*- or a *p*-position to one of the nitro-groups present in the molecule. Recent qualitative observations of interest show the remarkably high reactivity of *o*-bromobenzoic acid in a number of reactions,[91] and the removal of the nuclear chlorine in chlorobenzenetrisulphonanilide by aniline.[92] Mention may also be made of a valuable review of the literature concerning all kinds of reaction involving displacement of a group from the benzene ring.[93]

The underlying principles of these processes from the point of view of the electronic theory have been briefly discussed by Ingold.[94] The effective reagents are not the positive ions of ordinary substitution which seek negative centres, but groups such as NR_2, OH, OR, SR, SCN which are *positive*-centre-seeking. The normal orientation laws are therefore reversed. A group such as Me which repels electrons ($+I$ and $+D$ effects) will have a deactivating influence and one such as NO_2 which attracts electrons will activate ($-I$, $-D$ effects). Moreover the nitro-group will have a powerful conjugative or tautomeric ($-T$) effect which will operate by causing a local positive charge increasing at the demand of the reagent. The distribution of these charges in the ring will be the same as in ordinary orientation, that is to say, the effects will appear in the *o*- and *p*-positions but not in the *m*-position. The direct effect (D), however, represents the influence of a diminishing field in space and will vary in the order $o>m>p$.

At the moment of reaction a halogen atom may be regarded as assisting in the capture of the attacking negative ion by the influence of its own attraction for the electrons of the carbon atom to which it is attached, the process culminating in the transfer of
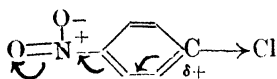
[88] *Ber.*, 1909, **42**, 601; *A.*, 1909, i, 232; *Annalen*, 1911, **379**, 152; *A.*, 1911, i, 329.

[89] J. Kenner and collaborators, *J.*, 1914, **105**, 2717; 1920, **117**, 852; 1921, **119**, 1047, 1053; 1922, **121**, 489, 675; 1923, **123**, 1260, 2296; 1925, **127**, 2343; 1927, 580; *A.*, 1927, 456.

[90] *Ann. Reports*, 1926, **23**, 137; 1928, **25**, 115; also R. J. W. Le Fèvre, S. L. M. Saunders, and E. E. Turner, *J.*, 1927, 1168; *A.*, 1927, 660.

[91] W. R. H. Hurtley, *J.*, 1929, 1870; *A.*, 1294.

[92] W. Davies and (Miss) E. S. Wood, *J.*, 1928, 1122; *A.*, 1928, 746.

[93] M. P. de Lange, *Rec. trav. chim.*, 1926, **45**, 19; *A.*, 1926, 278; compare J. J. Sudborough and J. V. Lakhumalani, *J. Indian Inst. Sci.*, 1915, **1**, 133.

[94] *Rec. trav. chim.*, 1929, **48**, 808.

the negative charge of the reagent ion across the atom in question to the chlorine which is being ejected as an ion.

A negative substituent may, however, sometimes enter the nucleus in the absence of halogen, hydrogen being replaced in a position conforming to the same inverted law of orientation. The following may be regarded as cases of this kind : the conversion of nitrobenzene by potassiocarbazole into p-nitrophenylcarbazole ;[95] the ready oxidation of resorcinol to phloroglucinol and of s-trinitrobenzene to picric acid ; the introduction of either one or two amino-groups into the molecules of m-dinitrobenzene and s-trinitrobenzene by the action of hydroxylamine in the presence of sodium ethoxide.[96]

Positive poles, being highly efficient as m-directive groups in normal substitution,[97] should also activate halogens in the o- and p-positions, and there is considerable evidence in the literature which is satisfactorily explained in this manner. For instance, the partial (and reversible) conversion of tribromoaniline into trichloroaniline by concentrated hydrochloric acid at $200°$ [98] is no doubt due to a halogen atom becoming activated by the free pole in the resulting salt, assisted in each case by the inductive and direct effects of the other halogen atoms. Another set of cases of the same kind is presented by the so-called isomeric change of halogenated diazonium salts discovered by Hantzsch.[99] The diazonium ion is a very powerful activator and nuclear halogen is rapidly displaced from it by the negative ion of the salt or any other negative ion provided. Thus diazotised tribromoaniline is easily converted into a trichlorobenzenediazonium salt reducible to s-trichlorobenzene, and p-chloroaniline furnishes p-thiocyanobenzenediazonium thiocyanate. It will be noticed that the rapidity of these reactions is once again contrasted with the slowness of ordinary aromatic substitution controlled by a free positive pole. The general effect now hastens the reaction instead of retarding it.
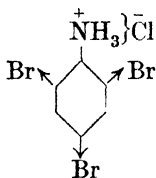
A reaction of the same kind which may be attributed to activation by a positively ionised carbon atom is that described by M. Gomberg and others [99a] in which tri-p-bromophenylmethyl chloride is partly transformed into di-p-chloro-p-bromotriphenylmethyl bromide in solution in liquid sulphur dioxide.

It is a property of halogen activated by electron-attracting groups to suffer ready removal by reduction, and it was recognised by H.

[95] R. Robinson, *Chem. and Ind.*, 1925, **44**, 117.

[96] J. Meisenheimer and E. Patzig, *Ber.*, 1906, **39**, 2533; *A.*, 1906, i, 652.

[97] *Ann. Reports*, 1926, **23**, 130.

[98] R. Wegscheider, *Monatsh.*, 1897, **18**, 329; *A.*, 1897, i, 557.

[99] J. C. Cain, " Diazo-Compounds," 2nd Ed., 1920, pp. 75–81.

[99a] *Ber.*, 1909, **42**, 412; *A.*, 1909, i, 144.

Burton and J. Kenner [1] that the ready elimination of halogen from such substances as 4-bromo-m-phenylenediamine occurs in the salt of the base, in which it is clear that two positive poles may jointly activate the halogen.

Comparative reactivities of nuclear halogen. A reaction velocity coefficient represents a fact concerning one reaction under certain experimental conditions : for different reactions or divergent conditions, the same two substances may possess widely differing comparative reactivities. Nevertheless, when two reactions are of similar polar type, the results will tend to be similar, and this is true on the whole for the reactions of activated nuclear halogens with sodium alkyloxides and organic amines studied by A. F. Holleman in a series of papers.[2] The more important general conclusions drawn with reference to the polychlorobenzenes and polychloro-mono- and -di-nitrobenzenes are that chlorine atoms exert an activating influence and that this is most effective from the m-position, but that it is slight compared with the strong effect of every nitro-group on chlorine atoms in op-positions. Thus m-dichloro-benzene is the most reactive of the three dichlorobenzenes, and s-trichlorobenzene of the isomeric trichlorobenzenes. p-Chloronitro-benzene is more reactive than its *ortho*-isomeride (p-, 7·2 ; o-, 1·9) and the introduction of each of two successive extra chlorine atoms into the nucleus raises the velocity 13—14 times. This preferential m-activation by chlorine was to be expected : the chlorine atom differs from the nitro-group in having a conjugative effect ($+T$) which must hinder the reaction under discussion and so leave the effect in the m-position greatest.

In such reactions it is usual for an iodine atom to react less readily than similarly situated bromine or chlorine [3, 4] and the same seems to be the case in a comparison of the speeds of dissolution of magnesium by aryl bromides and iodides under Grignard conditions.[5] The lower inductive effect and smaller tendency to pass into the anionic form characteristic of iodine as compared with bromine are consistent with this difference, but the comparison of chlorine and bromine is a more complicated point. The same comparison was made by A. H. Rheinlander [6] in a careful study of the reaction velocities of halogenonitrobenzenes with sodium ethoxide and bases. The bimolecular velocity coefficients at 50° for the reactions of

[1] *J.*, 1922, **121**, 679.

[2] *Rec. trav. chim.*, 1915, **35**, 1 ; 1918, **37**, 195 ; 1920, **39**, 435, 736 ; 1921, **40**, 67 ; *A.*, 1916, i, 22 ; 1918, i, 216 ; 1920, i, 538 ; 1921, i, 102, 167.

[3] H. Franzen and E. Bockhacker, *Ber.*, 1920, **53**, *B*, 1174 ; *A.*, 1920, i, 604.

[4] A. Brewin and E. E. Turner, *J.*, 1928, 332 ; *A.*, 1928, 402.

[5] H. W. Rudd and E. E. Turner, *ibid.*, p. 686 ; *A.*, 1928, 504.

[6] *Ibid.*, 1923, **123**, 3099.

sodium ethoxide with the three bromonitrobenzenes were $k \cdot 10^5 =$ 6·3, 0·0, and 12·2 for o-, m-, and p- : for the chloro-, bromo-, and iodo-2 : 4-dinitrobenzenes with aniline, $k \cdot 10^3 = 2·75, 4·21$, and 1·23 respectively.

In connexion with the comparison in reactivity of iodine with chlorine or bromine it is of interest that the group OR of polynitroaryl ethers is also displaced by amines,[7] and it may be concluded that in the series Cl, I, OPh, OMe, NR_2 a group may be used to displace any one which precedes it, the ease of reaction increasing with the distance apart in the series. It is clear that the tendency of the last four groups to form the undissociated hydrogen compounds HI, HOPh, HOMe and HNR_2 increases in that order, the series being one of increasing proton-affinity.

An estimate of the comparative activating effects of the groups $NO_2 > SO_3H > CO_2H$ has been made by W. Davies and (Miss) E. S. Wood,[8] who find the ratios 70,000 : 1 : $\frac{1}{3}$ for these groups in reactions between mono-, di-, and tri-substituted chlorobenzenes with aqueous-alcoholic potassium hydroxide. The nitro-group is also stated to have the property of making other groups more effective activators. For instance, the introduction of the group CO_2H or SO_3H into o-chloronitrobenzene in the p-position to the halogen raises the reactivity 4·4 or 16 times respectively, although the reactivity of p-chlorobenzoic and p-chlorosulphonic acids cannot be detected. It is probable, however, that the latter reactivities, if they could be measured, would show a similar increase as compared with that of chlorobenzene.

The remarkable influence of the nitro-group is no doubt connected with its capacity to form addition compounds, a point of view particularly stressed by Kenner, who has established the fact that reaction is often inhibited by steric hindrance, not at the atom or group displaced, but at the nitro-group which activates it. A clear case of this kind is presented by H. Lindemann and A. Pabst,[9] who have examined the effect on the speed of reaction with aniline of introducing a methyl group in various positions into chloro-2 : 4-dinitrobenzene. The following are the values of relative reactivity :

Parent compound.	5 Me-.	6 Me-.	3 Me-.
0·18	0·05	0·01	0·00

The general depression of reactivity by the introduction of the methyl group is in accordance with its electron-repelling properties. The authors are at a loss to account for the complete inertness of the 3-methyl derivative, but it may be regarded as due to steric hindrance to the formation of any addition compound.

[7] W. Borsche, *Ber.*, 1923, **56**, *B*, 1488 ; *A.*, 1923, i, 780.
[8] *Loc. cit.* (ref. 92).   [9] *Annalen*, 1928, **462**, 24 ; *A.*, 1928, 877.

The exact nature and function of such an addition compound is a problem of importance and has been discussed recently by A. Brewin and E. E. Turner.[10] The following statement is based on their views.

The facts may be explained by the conception that a reagent such as sodium ethoxide or an amine first forms an addition [11] compound at the nitro-group having the structure (I) or (II), in which the

(I.)   (II.)
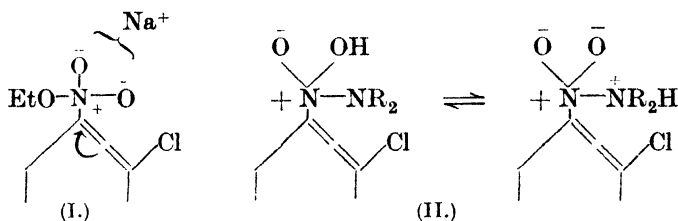
altered nitro-group may be assumed to have enhanced activating power. A second molecule of amine or an ethoxide ion then attacks this complex at the carbon atom carrying the chlorine, and the reaction proceeds to completion : or, as an alternative possibility, the radical OEt or NR_2 may migrate to the o-carbon atom by a purely intramolecular change.

II. *Side-chain Reactivity.*—This subject has been discussed in the last two Reports.[12] The following account is supplementary, with special reference to the question of displacement of chlorine by iodine or hydroxyl.

A very elegant method of measurement has been devised and applied by J. B. Conant, W. R. Kirner, and their colleagues to determine the velocity of the reaction $RCl + I' \longrightarrow RI + Cl'$ for a variety of substances at two temperatures.[13] There is consequently available an exceptionally large set of accurate data. Some of these results are in the table below, the figures being reactivities of various substances $R(CH_2)_nCl$ for this reaction in acetone at 50° referred to that of n-butyl chloride as unity.

R.	n = 0	1	2	3	4	5	6	7
H	—	—	2·52	1·08	1·00	1·35	1·30	1·25
Ph	—	197	1·12	1·72	1·49	1·42	1·46	1·40
Ph·CO	ca. 2200	ca. 10⁵	86·7	372	—	—	—	—
CO₂Et	42	1720	1·61	1·65	1·35	—	—	—
Ph·S	—	—	0·56	2·74	—	—	—	—
Me·S	—	—	1·52	2·52	—	—	—	—

[10] *J.*, 1928, 334; *A.*, 1928, 402.

[11] Compare G. M. Bennett and G. H. Willis, *J.*, 1929, 259; *A.*, 436.

[12] *Ann. Reports*, 1927, **24**, 155; 1928, **25**, 146.

[13] *J. Amer. Chem. Soc.*, 1924, **46**, 233; *A.*, 1924, i, 273; J. B. Conant and R. E. Hussey, *ibid.*, 1925, **47**, 476, 488; *A.*, 1925, i, 493, 494; W. R. Kirner, *ibid.*, 1926, **48**, 2745; 1928, **50**, 2446; *A.*, 1926, 1224; 1928, 1214; W. R. Kirner and G. H. Richter, *ibid.*, 1929, **51**, 3409.

E 2

The general tendency of the variation of reactivity with structure is indicated by the statement (which also involves data not given in the table) that $R \cdot CH_2Cl$ has a velocity of reaction with iodides which diminishes in the following order with variation of R : $Ph \cdot CO > Me \cdot CO > CN > CO_2Et > MeO > AcO > Ph \cdot CO \cdot CH_2 \cdot CH_2 > Ph > CH_2 \colon CH > C_3H_7$. For comparison with the figures for n-alkyl chlorides the relative values of *iso*propyl chloride, *tert.*-butyl chloride, and *cyclo*hexyl chloride, 0·015, 0·018, and <0·0001 respectively, are of interest. The order of the above series is identical with that found by A. Slator [14] for the reaction of a few of the corresponding iodides with sodium thiosulphate, but not with that found by H. T. Clarke for reactions of bromides with pyridine.[15] It is immediately noticeable that the order in the series is one of diminishing electron-affinity, as indicated by strengths of acids or m-direction in aromatic substitution, and this is so much the reverse of what might be expected in view of the elimination of chlorine as a *negative ion* that Conant concluded that the results could not be reconciled with the electronic theory.

It is equally true, however, that the reaction involves the introduction of a negative iodine ion *into* the molecule, and it has been pointed out, with particular reference to aryl β- and γ-chloroalkyl sulphides, that the explanation may lie in the formation of a complex between the chloride and an iodine ion.[16] This will be hastened by any recession of electrons from the carbon atom carrying the chlorine, and, if the subsequent liberation of the chlorine ion is very rapid, the observations are explained. This view is supported by the fact that structural changes which increase the speed of this reaction diminish that of hydrolysis. For instance, the γ-chloro-sulphide reacts faster with iodide but more slowly in hydrolysis than the corresponding β-chloro-sulphide, and the introduction of a nitro-group accelerates the former but retards the latter reaction. The following comparison of the values of relative reactivity found by Conant and by Olivier for the two reactions further illustrates the point. In each series the values refer to that for benzyl chloride taken as unity.

	o-NO$_2$.	m-NO$_2$.	p-NO$_2$.	o-Cl.	p-Cl.	o-Br.	p-Br.
Iodide (Conant) [17]	9·2	4·0	7·0	3·64	2·80	392	244
Hydrolysis (Olivier) [18]	0·084	0·090	0·074	0·355	0·62	0·286	0·50

An interpretation of the whole of these data from this point of

[14] *J.*, 1904, **85**, 1286; 1905, **87**, 481; 1909, **95**, 93.
[15] *J.*, 1910, **97**, 416; 1911, **99**, 1927; 1912, **101**, 1788; 1913, **103**, 1689.
[16] G. M. Bennett and W. A. Berry, *J.*, 1927, 1676; *A.*, 1927, 871.
[17] Calculated from Conant's data, *loc. cit.*
[18] *Ann. Reports*, 1927, **24**, 156.

view is possible. There is an observed alternation in the reactivity of successive homologues in several cases, which Conant and Kirner attribute to an effect transmitted from the group R along the saturated chain. This will be regarded by many as improbable wherever the chain in question exceeds three carbon atoms at the most in length, as is clear from the results of nitration of the substances $Ph(CH_2)_n \cdot NMe_3X$,[19] from the values [20] of the second dissociation constants of dibasic acids, and from the study of dipole moments.[21] There are other possible factors such as a direct effect of R upon the group CH_2Cl through space.[22]

The following additional data relating to the speeds of hydrolysis have been reported by Olivier [23] for the 2 : 6-, 3 : 4-, and 3 : 5-dibromobenzyl chlorides : 0·120, 0·207, and 0·070 respectively, referred to benzyl chloride as unity. A closely related set of measurements is that of J. F. Norris and his assistants [24] for the reversible first-order reaction of substituted benzhydryl chlorides (α-phenylbenzyl chlorides) with ethyl alcohol at 25°. Relative values, referred to benzhydryl chloride as unity, are :

Substituent.	Velocity.	Substituent.	Velocity.	Substituent.	Velocity.
o-Cl	0·01	o-Me	2·9	p-Ph	12·8
m-,,	0·045	m-,,	2·1	p-PhO	31·6
p-,,	0·42	p-,,	16·2	o-MeO	93
pp'-Cl₂	0·15	pp'-Me₂	413	p-MeO ca. 1200	
p-Br	0·33	p-Et	20·9		

Values for α-naphthylphenylmethyl chloride and benzylphenylmethyl chloride are 7·2 and 0·0004 respectively.

A comparison of these figures with those of Olivier for the benzyl chlorides shows that the effects of substituents are parallel in the two series, except that the values for o-substituted benzhydryl chlorides show a special depression which may fairly be regarded as due to steric hindrance.

In an interesting study of the action of aqueous sodium hydroxide upon benzhydryl chloride [25] it is shown that the reaction is of the first order and practically independent of the added alkali. Although

[19] Ann. Reports, 1926, 23, 131.
[20] R. Gane and C. K. Ingold, J., 1929, 1691; A., 1144; compare H. J. Lucas and H. W. Moyse, J. Amer. Chem. Soc., 1925, 47, 1459; A., 1925, i, 770.
[21] C. P. Smyth, ibid., 1929, 51, 2380; A., 1128.
[22] G. M. Bennett and A. L. Hock, J., 1927, 477; A., 1927, 355; G. M. Bennett, F. Heathcoat, and A. N. Mosses, J., 1929, 2567.
[23] S. C. J. Olivier, Rec. trav. chim., 1929, 48, 227; A., 405; compare Ann. Reports, 1927, 24, 156.
[24] J. Amer. Chem. Soc., 1928, 50, 1795, 1804, 1808, 1813; A., 1928, 1000.
[25] A. M. Ward, J., 1927, 445, 2285; 1929, 1541; A., 1927, 453, 1061; 1929, 1072.

this is consistent with Nef's suggestion [26] of the formation of a free bivalent carbon radical thus,

$$CHPh_2Cl \xrightarrow[-HCl]{slow} CPh_2 < \xrightarrow[+ROH]{fast} CHPh_2 \cdot OR,$$
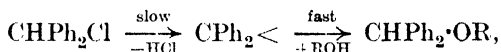
the author points out that the following scheme fits the facts equally well :

$$CHPh_2Cl \xrightarrow{slow} CHPh_2^+ + Cl^- \text{ and } CHPh_2^+ + OR^- \xrightarrow{fast} CHPh_2 \cdot OR.$$
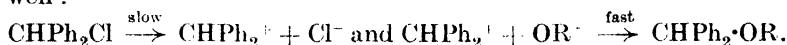
The ready reaction of triphenylmethyl chloride in a similar manner makes the latter explanation the more acceptable. Similar bivalent carbon radicals have also been postulated as intermediates in some reactions of p-nitrobenzyl chloride and related substances. The former is converted by alcoholic alkali into pp'-dinitrostilbene and by aldehydes $Ar \cdot CHO$ into substituted ethylene oxides of the

type $C_6H_4(NO_2) \cdot CH \overset{O}{\overset{\diagup \diagdown}{—}} CHAr$.[27] A simpler explanation may be found, however, in the enhanced reactivity of the hydrogen atoms of the methylene group of the benzyl chloride owing to the electron attraction of the halogen atom,[28] the stilbene being formed through the intermediate $C_6H_4(NO_2) \cdot CH_2 \cdot CHCl \cdot C_6H_4 \cdot NO_2$. The known formation of bromodiphenacyl from phenacyl bromide and alcoholic sodium ethoxide illustrates the type of reaction :

$$2Ph \cdot CO \cdot CH_2Br \xrightarrow{NaOEt} Ph \cdot CO \cdot CHBr \cdot CH_2 \cdot COPh.$$
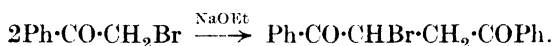
In conclusion, attention may be directed to two recent examples of " positive " reactivity of halogen, namely, of the chlorine atom in the SO_2Cl groups of trichloromethanesulphonyl chloride [29] and of dinitrobenzenesulphonyl chloride.[30]

Stereoisomerism of Polycyclic Aromatic Compounds.
(Continued from *Ann. Reports*, 1928, **25**, 114—118.)

The results recorded in this field during the year provide further confirmation of current theories of the structure of diphenyl, and the disproof of a number of cases of stereoisomerism among other polycyclic substances is also in gratifying agreement with the indications which physical measurements have given concerning the structure of the benzene nucleus.

Diphenyl Isomerism.—The view expressed by Mills [31] that the

[26] J. U. Nef, *Annalen*, 1897, **298**, 234; *A.*, 1898, i, 102.

[27] E. Bergmann and J. Hervey, *Ber.*, 1929, **62**, *B*, 893; *A.*, 695.

[28] E. Kleucher, *ibid.*, p. 2587.

[29] J. F. Durand and R. Naves, *Bull. Soc. chim.*, 1927, [iv], **41**, 632; *A.*, 1927, 645.

[30] A. T. Dann and W. Davies, *J.*, 1929, 1050; *A.*, 921.

[31] *Ann. Reports*, 1926, **23**, 124.

occurrence of enantiomorphism in substituted diphenyls arises from the purely mechanical obstruction of rotation by (not less than three) *ortho*-situated groups has been shown to be correct by the isolation of optically active 3 : 3'-diaminodimesityl (I) by W. W. Moyer and R. Adams,[32] the blocking groups being identical and of the least polar type possible. The following have also been resolved into optically active forms : 6 : 6'-dimethoxydiphenic acid,[33] 2 : 2'-diamino-1 : 1'-dinaphthyl,[34] 2 : 2'-dihydroxy-1 : 1'-dinaphthyl-3 : 3'-dicarboxylic acid,[35] and 1 : 1'-dianthraquinonoyl-2 : 2'-dicarboxylic acid (II).[36]
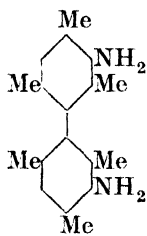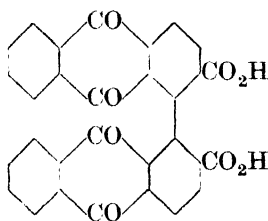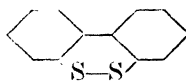
(I.)   (II.)   (III.)

A number of other substances [37] have resisted resolution in conformity with theoretical expectation, of which 5 : 5'-dinitro- and 5 : 5'-dibenzamido-diphenic acids may be noted.[38]

On the other hand, a few more recorded observations which seemed to provide evidence in favour of the Kaufler formula for diphenyl have received satisfactory alternative explanations.[39] An interesting piece of direct evidence against the formula is furnished by H. J. Barber and S. Smiles,[40] who have oxidised 2 : 2'-dithioldiphenyl to a crystalline diphenylene 2 : 2'-disulphide (III) but find that the 3 : 3'- and 4 : 4'-dithioldiphenyls yield no cyclic disulphide.

A stereochemical explanation has been suggested [41] of the existence of an unexpected isomeride formed from 5'-chloro-2'-hydroxy-2-benzoyl-*m*-toluic acid by the action of sulphuric acid, but it may be asserted with confidence that the difference between the two

[32] *J. Amer. Chem. Soc.*, 1929, **51**, 630; *A.*, 437.

[33] J. Kenner and H. A. Turner, *J.*, 1928, 2340; *A.*, 1928, 1244.

[34] R. Kuhn and P. Goldfinger, *Annalen*, 1929, **470**, 183; *A.*, 804; L. Mascarelli, *Gazzetta*, 1928, **58**, 627; *A.*, 181.

[35] W. M. Stanley and R. Adams, *Rec. trav. chim.*, 1929, **48**, 1035; *A.*, 1298.

[36] R. Kuhn and O. Albrecht, *Annalen*, 1928, **464**, 91; *A.*, 1928, 1015.

[37] J. F. Hyde and R. Adams, *J. Amer. Chem. Soc.*, 1928, **50**, 2499; *A.*, 1928, 1234.

[38] F. Pufahl, *Ber.*, 1929, **62**, [B], 2817.

[39] R. J. W. Le Fèvre, *J.*, 1929, 733; *A.*, 705.

[40] *J.*, 1928, 1141; *A.*, 1928, 769.

[41] M. Hayashi, *J.*, 1927, 2516; *A.*, 1927, 1187.

substances must be of another kind.   The author regards them alternatively as structural isomerides and writes the conversion thus :
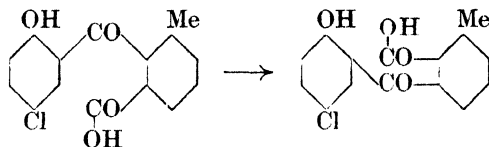
Chlorohydroxymethylanthraquinone is also formed from the acid under the influence of sulphuric acid.   A more probable explanation of the facts would therefore seem to be given by the following scheme, in which it is assumed that the anthraquinone formation is reversible in two ways :
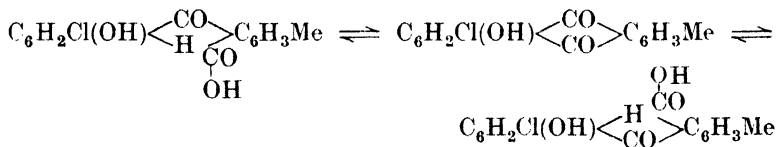
This implies a constitution for the second acid different from that suggested by the author.

Isomeric Dimethyl-2-phenylnaphthylenediamines.—The intriguing problem of the existence of two isomeric forms of NN'-dimethyl-2-phenylnaphthylene-1 : 3-diamine has been re-examined [42] and the earlier work of N. Lees and J. F. Thorpe [43] confirmed and amplified. The substance (IV) occurs in α- and β-forms, of which the α-base yields only monoacyl, the β-base diacyl derivatives.   The dinitroso-derivatives of the two have now been found to be one and the same substance, from which the β-base can be recovered.   Both α- and β-bases resisted attempts to resolve them into optically active forms. The authors state that if all the nuclei and substituents lie in one plane the phenyl group is prevented from rotating, but it should be noticed that even if this were the case no enantiomorphism would be expected.   They conclude that the α- and β-forms are best represented as *cis*- and *trans*-isomerides, the whole being supposed to lie in one plane (V, VI).
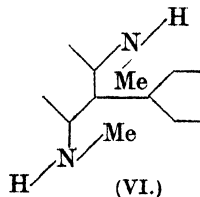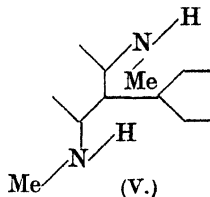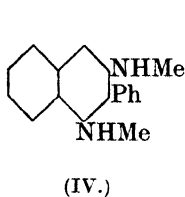
[42] C. S. Gibson, W. S. Kentish, and J. L. Simonsen, *J.*, 1928, 2131; *A.*, 1928, 1128.   [43] *J.*, 1907, **91**, 1296.

A more satisfactory suggestion, put forward simultaneously by W. S. Kentish [44] and (Miss) M. S. Lesslie and E. E. Turner,[45] is that the α-dimethyl base is a structurally isomeric methylimino-compound derived from a tautomeric form of the parent diamine : α-base (·NHMe, :NMe), β-base (·NHMe, ·NHMe). This at once accounts for the formation of the monoacyl derivatives of the former and diacyl derivatives of the latter. The supposition that the phenyl group in these compounds cannot rotate is a misapprehension : this would only be the case if the methylamino-groups were fixed in definite positions, a supposition for which there is no justification. In point of fact, if *either* the phenyl *or* the NHMe groups are free to rotate at all, there can be no effective inhibition.

No question arises as to the structure of the β-base, which is (IV). There is some difference of opinion, however, regarding the α-isomeride. Kentish writes it as (VII); but in view of the failure to resolve it into enantiomorphs Lesslie and Turner prefer the formula (VIII). These authors show that the known reactions of the parent base indicate at least three tautomeric forms (IX, X, XI); but the formula (IX) is clearly demonstrated as the normal one by their resolution of the base into optically active forms.

$$(VII.) \qquad \begin{array}{c} CH \\ C{-}NHMe \\ C{<}^{Ph}_{H} \\ C \\ \| \\ NMe \end{array} \qquad\qquad (VIII.) \qquad \begin{array}{c} CH_2 \\ C{-}NMe \\ CPh \\ C \\ NHMe \end{array}$$

$$(IX.) \quad \begin{array}{c} CH \\ C{\cdot}NH_2 \\ CHPh \\ C{:}NH \end{array} \;\rightleftharpoons\; (X.) \quad \begin{array}{c} NH_2 \\ Ph \\ NH_2 \end{array} \;\rightleftharpoons\; (XI.) \quad \begin{array}{c} CH_2 \\ C{:}NH \\ CPh \\ C{\cdot}NH_2 \end{array}$$
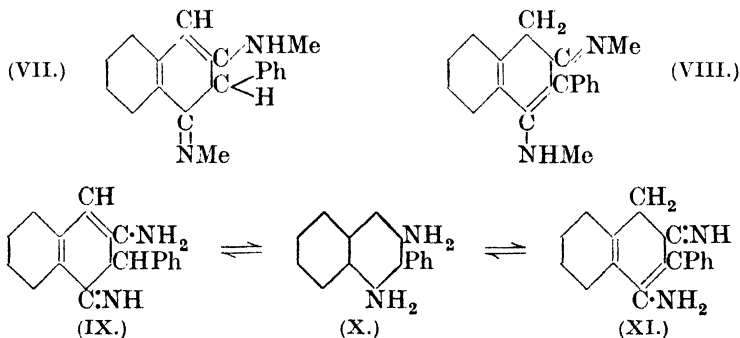
Isomerism attributed to Inclined or Non-planar Nuclei.—In the course of their extensive researches into the action of alkali metals upon organic substances [46] Schlenk and Bergmann isolated a number of substances which were unexpected according to classical stereochemical ideas. On the hypothesis that in polynuclear systems the planes of adjacent rings are inclined to one another at an angle, they regarded the existence of these substances as due to a kind of *cis–trans* isomerism. For instance, there were described two each of 1 : 2 : 3-triphenyl- and 1 : 1 : 3-triphenyl-hydrindenes, 1 : 2 : 3-triphenylnaphthalenes, 9 : 10-diphenylanthracenes, 9 : 10-di-

[44] *J.*, 1929, 1169; *A.*, 923.   [45] *Ibid.*, p. 1512; *A.*, 1061.
[46] *Ann. Reports*, 1928, **25**, 152; W. Schlenk and E. Bergmann, *Ber.*, 1929, **62**, [B], 745; E. Bergmann and H. Mark, *ibid.*, p. 750; *A.*, 688, 689.

phenyldihydroanthracenes, 9-benzhydrylfluorenes, and 9-phenyl-9-benzylfluorenes; three isomeric forms were found of 9 : 10-dihydroanthracenedicarboxylic acid and of diphenyldihydroanthracenedicarboxylic acid.

The interpretation given of the existence of these substances is illustrated by the annexed formula for a substituted 9 : 10-dihydroanthracene. The outer rings are supposed to be inclined at an angle to the central nucleus, each being bent to the same side of the plane of the latter. This will clearly have the effect of differentiating between the two directions perpendicular to that plane and the formula should represent three stereoisomerides.

To account for the existence of two diphenylanthracenes (unreduced) on this view, it would be necessary to make the improbable assumption that in them the phenyl nuclei are not co-axial with the central nucleus. In further support of these ideas, 2 : 3-diphenylindone was stated to be resolved into optically active forms by means of bornylamine.
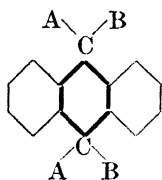
These announcements have been followed by similar ones from other quarters involving phenylindene derivatives,[47] and pairs of dianthranyls and phenylbenzhydryldichlorodihydroanthranols.[48]

S. Haeckel and H. Mark [49] explain the new isomerism by assuming a multiplanar formula for the benzene ring similar to that of Bragg. Recent physical work on benzene derivatives discussed above (p. 126) makes both Schlenk's and Haeckel's explanations improbable.

It is consequently reassuring to find that a number of the unexpected isomerides have already been explained away. An attempt to repeat the resolution of diphenylindone was unsuccessful : [50] the second forms of 9 : 10-dihydroanthroic acid,[51] benzhydrylfluorene and diphenyldiphenylene-ethylene have been found to be mixtures,[52] and the isolation of the second fluorene-9-carboxylic acid and 9-phenyl-9-benzylfluorene could not be repeated.[53] The substance described as a stereoisomeric 1 : 1 : 3-triphenylhydrindene is a structural isomeride.[54] In addition it may also be pointed out, with reference to the two cases of isomerism discussed by Barnett and Goodway, (a) that it is difficult to believe that the *iso*dianthranyl has been given the correct formula, since in its preparation by

[47] C. Moureu, C. Dufraisse, and M. Badoche, *Bull. Soc. chim.*, 1928, [iv], **43**, 1381 ; *A.*, 318.

[48] E. de B. Barnett and N. F. Goodway, *J.*, 1929, 20, 813 ; *A.*, 312, 700.

[49] *J. pr. Chem.*, 1929, [ii], **122**, 182, 349 ; *A.*, 1050.

[50] J. Meisenheimer and W. Theilacker, *Annalen*, 1929, **469**, 26 ; *A.*, 448.

[51] H. Meerwein and A. Migge, *Ber.*,1929, **62**, [*B*], 1046 ; *A.*, 696.

[52] A. Kliegl, *ibid.*, p. 1327 ; *A.*, 812.

[53] R. E. Schmidt, B. Stein, and C. Bamberger, *ibid.*, p. 1890 ; *A.*, 1054.

[54] K. Ziegler and F. Crossmann, *ibid.*, p. 1768 ; E. Haack, *ibid.*, p. 1771 ; *A.*, 1054.

reduction of benzhydrylanthrone an extra carbon atom would seem to have been inexplicably introduced into the molecule, and (b) that the analytical figure for the second phenylbenzhydryldichloro-dihydroanthranol would agree equally well with the very probable supposition that the substance is not an isomeride but results from the loss of one molecule of water.

It therefore seems likely that all these cases of unexpected isomerism were imaginary, and it might at first sight appear that much labour had been wasted. But this is not entirely true. When the disproof of the supposed isomerism is complete in all instances, there will be a mass of evidence which will support the conception that the rings of polynuclear hydrocarbons are in a single plane.

Natural Products.

(Continued from *Ann. Reports*, 1927, **24**, 119—128.)

I. *The Terpene Group.*—(1) *Monoterpene compounds.* The synthesis of norpinic acid, recently announced, completes at last the logical proof of the structure of pinene. Norpinic acid was obtained as the ultimate product of degradation of the terpene in 1896 by A. von Baeyer,[55] who gave it the *cyclo*butane formula

$$\text{Me}_2\text{C} \underset{\text{CH·CO}_2\text{H}}{\overset{\text{CH·CO}_2\text{H}}{\diamondsuit}} \text{CH}_2 \quad ,$$
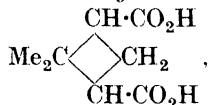
but many attempts to synthesise it have been unsuccessful.[56] The difficulty has now been surmounted by C. A. Kerr,[57] who condensed the sodium derivative of the Guareschi imide (I) with methylene iodide. The resulting bridged-ring imide (II) was converted by alkaline hydrolysis into 2 : 2-dimethyl*cyclo*butane-

$$\text{(I.) Me}_2\text{C} \underset{\text{CH(CN)·CO}}{\overset{\text{CH(CN)·CO}}{\diamondsuit}} \text{NH} \longrightarrow \text{Me}_2\text{C} \underset{\text{C(CN)—CO}}{\overset{\text{C(CN)—CO}}{\diamondsuit}} \text{CH}_2 \text{NH (II.)}$$
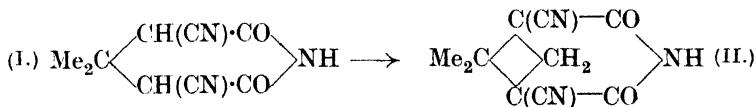
1 : 1 : 3 : 3-tetracarboxylic acid, which was decarboxylated to give *trans*-norpinic acid.

The oxidation of terpenes with Beckmann's chromic acid mixture has yielded interesting results, and the method may find application for identifying the constituents of terpene mixtures. α-Terpinene gives mainly dimethylacetonylacetone.[58] From *l*-limonene there is obtained the keto-lactone $C_{10}H_{16}O_3$ prepared by Wallach from terpineol; and among the products from α-phellandrene are two

[55] K. Ziegler and F. Grossman, *Ber.*, 1896, **29**, 19071; *A.*, 1896, i, 620.

[56] G. R. Clemo and K. N. Welch, *J.*, 1928, 2621; *A.*, 1928, 1252.

[57] *J. Amer. Chem. Soc.*, 1929, **51**, 614; *A.*, 445.

[58] T. A. Henry and H. Paget, *J.*, 1928, 70; *A.*, 1928, 295.

keto-lactones (III; IV), each of which is further degraded to
l-α-isopropylsuccinic acid.

$$\begin{array}{cc}
\text{COMe} & \text{COMe} \\
\end{array}$$

COMe

CH₂   CO
   O
HC   CH₂
  CH
  C₃H₇(β)
(III.)

COMe

CH
  O
CO   CH₂
  CH
  C₃H₇(β)
(IV.)
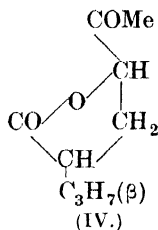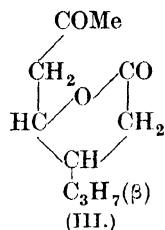
By the same method, both d-Δ³- and d-Δ⁴-carene give l-$trans$-caronic acid in good yield.[59] The production of this acid from a natural mixture would therefore be proof of the presence of carene. Another point of considerable interest concerns the configuration of the caronic acid isolated : the carene must have the cis-structure with respect to the $cyclo$propane ring, and therefore it is clear that molecular rearrangement occurs at some point in the course of the degradation.

(2) *Sesquiterpene compounds.* Work in this field during the past two years has continued to be fruitful : the structures of bisabolene and zingiberene have been elucidated and the chemistry of cedrene has been largely accounted for.[60]

The formation of bisabolene by the action of acids on nerolidol indicated, by analogy with the case of linalool, the formulæ (I, II, and III) as possible for the terpene, the point of uncertainty being the position of one ethylenic linkage. All three formulæ are consistent with (IV) as the trihydrochloride.

CH₃   CH₂   CH₃
   CH₃   CH₃   CH₃
CH₃ CH₃   CH₃ CH₃   CH₃ CH₃
(I.)   (II.)   (III.)

Cl CH₃   CH₃
          Cl
          CH₃   CH₃
Cl
CH₃ CH₃   CH₃ CH₃
(IV.)   (V.)
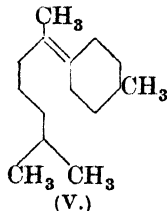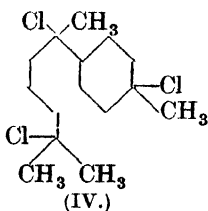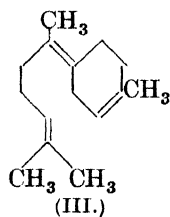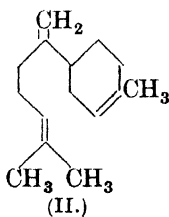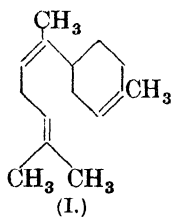
[59] C. S. Gibson and J. L. Simonsen, *J.*, 1929, 305, 909; *A.*, 449, 819.
[60] L. Ruzicka and A. G. van Veen, *Annalen*, 1929, **468**, 133, 143; *A.*, 571, 572.

The hydrocarbon from opopanax oil is identical with that regenerated from the trihydrochloride and constitution (III) is assigned to it for the following reasons. Degradation by means of ozone produces acetone and lævulic and succinic acids, but this is consistent with any of the formulæ above. Decisive evidence was, however, obtained by examination of tetrahydrobisabolene (V) formed by catalytic reduction of the terpene. The slowness of addition of two more hydrogen atoms to yield a hexahydro-derivative is best accounted for by the formulæ (III) and (V) for bisabolene and its tetrahydro-derivative. This is proved by ozonolysis of the latter to β-methylheptan-ζ-one and 4-methyl*cyclo*hexanone. No diacetyl-valeric acid, formic acid or formaldehyde was detected such as would arise if any bisabolene of the structure (I) or (II) were present. Bisabolene yields on dehydrogenation a benzene derivative oxidis-able to terephthalic acid, formation of the naphthalene nucleus being hindered by the hemicyclic double bond.

Zingiberene has not the wide distribution in nature of bisabolene, having been obtained until recently only from ginger oil. Its discovery in the oil from the rhizomes of *Curcuma zedoaria*, Roscoe,[61] is therefore of considerable interest.

The crude terpene from ginger oil is shown to contain 20—30% of bisabolene by the isolation of its trihydrochloride and by the occurrence of acetone, lævulic and succinic acids among the products of ozonolysis.

Hexahydrozingiberene [62] is dehydrogenated over palladised charcoal to ζ-*p*-tolyl-β-methylheptane, which is oxidised by chromic acid to acetic, oxalic and terephthalic acids, the last in too large an amount to have arisen from the bisabolene present. As no tri- or tetra-carboxylic acid of benzene is produced, the carbon skeleton

(VI.)   (VII.)
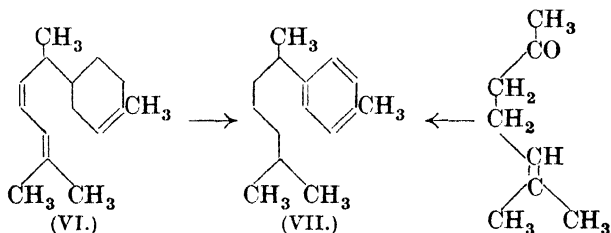
of zingiberene is proved to be the same as that of bisabolene, con-trary to earlier conceptions.[63] The dehydrogenation product (VII) was also synthesised by successive dehydration and catalytic

[61] B. S. Rao, V. P. Shintre, and J. L. Simonsen, *J. Soc. Chem. Ind.*, 1928, **47**, 171; *B.*, 1928, 799.

[62] F. W. Semmler and A. Becker, *Ber.*, 1913, **46**, 1814; *A.*, 1913, i, 743.

[63] *Ann. Reports*, 1927, **24**, 123.

reduction of the product from magnesium p-tolyl bromide and methylheptenone.

The complication due to the presence of bisabolene was avoided by condensing crude zingiberene with ethyl diazoacetate, the zingiberene (having conjugated double bonds) alone reacting to form the acid (VIII).[64] After successive hydrogenation and dehydrogenation of the ester, the product was oxidised to terephthalic acid. This provides a more conclusive proof of the carbon skeleton of the terpene.

The dihydrozingiberene obtained by reduction with sodium and alcohol yields some cadalene when heated with sulphur. Decomposition of its ozonide with permanganate gave an acid, $C_{12}H_{20}O_5$, isolated as its methyl ester. By the action of sodium hypobromite there resulted, after re-esterification, a trimethyl ester of the acid $C_{11}H_{18}O_6$. This completes the proof of structure, the acids having the constitutions (IX) and (X), and zingiberene (VI).
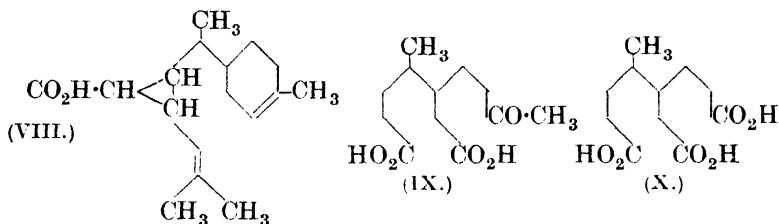
The investigation of cedrene is well advanced, although not yet complete.[65] The terpene is found in cedar-wood oil and is also produced artificially from the related alcohols cedrenol, cedrol, and ψ-cedrol.

The molecular refraction of cedrene and the saturated character of its tetrahydro-derivative show that it is tricyclic.[66] A ketone, cedrone, $C_{15}H_{22}O$, together with cedreneketonic acid,

$$C_{11}H_{18}(COMe)\cdot CH_2 \cdot CO_2H,$$
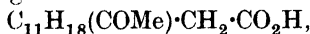
is afforded by the action of chromic anhydride in acetic acid. The production of the former may be regarded as analogous to the conversion of limonene into carvone and involves oxidation of $-CH\!:\!CH\cdot CH-$ to $-CH\!:\!CH\cdot CO-$. Further oxidation of cedreneketonic acid yields cedrenedicarboxylic acid, whereas ozonolysis of cedrone leads to norcedreneketonic acid, convertible by hypobromite into norcedrenedicarboxylic acid. The last acid must be formulated as

$$C_7H_{12}\!\!<\!\!\begin{array}{l}CMe\cdot CO_2H\\CH\cdot CH_2\cdot CO_2H\end{array} \quad \text{(or possibly } C_8H_{14}\!\!<\!\!\begin{array}{l}CH\cdot CO_2H\\CH\cdot CH_2\cdot CO_2H\end{array}),$$
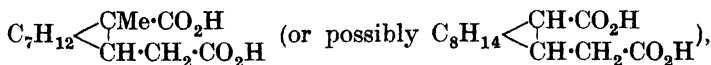
[64] H. Staudinger, O. Muntwyler, L. Ruzicka, and S. Seibt, *Helv. Chim. Acta*, 1924, **7**, 390; *A.*, 1924, i, 730.

[65] L. Ruzicka and J. A. van Melsen, *Annalen*, 1929, **471**, 40; *A.*, 932.

[66] F. W. Semmler and E. W. Mayer, *Ber.*, 1912, **45**, 1387; *A.*, 1912, i, 479.

for it differs from cedrenedicarboxylic acid in that the two carboxyl groups show unequal reactivity with respect to esterification and hydrolysis.

One carbomethoxy-group of the methyl ester of this acid reacts with magnesium methyl bromide, and the resulting carbinol, $C_7H_{12}{<}^{CMe·CO_2Me}_{CH·CH_2·CMe_2·OH}$, is oxidised to cedrocamphoric acid, $C_6H_{10}{<}^{CHMe·CO_2H}_{CO_2H}$. These results cannot be reconciled with formulæ for cedrene put forward by E. Deussen [67] and by Semmler, and they show that cedrene must be of the type (XI), or (XII) on the basis of the alternative formula of norcedrenedicarboxylic acid. The third ring of cedrene is present in the portion C_6H_{10} and can only be three- or four-membered. A formula such as (XIII) is therefore probable for cedrene.

(XI.)   (XII.)   (XIII.)
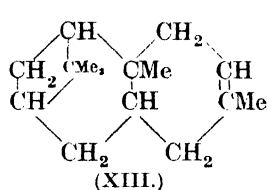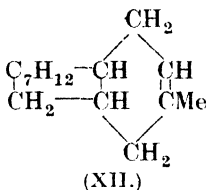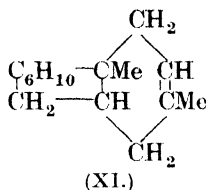
11. *Constituents of Kawa Root.*—The principal substances isolated from kawa root (*Piper methysticum*) are methysticin, ψ-methysticin, and yangonin and are found in the residues from the preparation of kawa-resin. The chemical nature of these and of the resin has been demonstrated in recent years by W. Borsche and his fellow-workers.

Yangonin was shown by E. Winzheimer [68] to be a dimethoxy-compound, $C_{15}H_{14}O_4$. It behaved as a lactone, and yangonic acid, which resulted from it by the action of alkali, lost carbon dioxide above its melting point to yield a neutral substance, yangonole.

A detailed study of yangonin [69] revealed properties characteristic of pyrones, such as the formation of oxonium salts with complex acids and of a pyridone by the action of ammonia. Hydrolysis afforded first yangonic acid, $C_{14}H_{14}O_5$, and then either *p*-methoxy-cinnamic and acetoacetic acids or anisylideneacetone and malonic acid. Dihydroyanganole, the product of catalytic reduction, was hydrolysed to anisylethyl methyl ketone and β-anisylpropionic acid.

Consequently the structure $MeO·C_6H_4·CH{:}CH·C{<}^{O·C(OMe)}_{CH—CO}{>}CH$

[67] *J. pr. Chem.*, 1927, [ii], **117**, 273; *A.*, 1928, 70.

[68] *Arch. Pharm.*, 1908, **246**, 338; *A.*, 1908, i, 804.

[69] W. Borsche and (Frl.) M. Gerhardt, *Ber.*, 1914, **47**, 2902; *A.*, 1915, i, 438.

was assigned to yangonin, that is, 2-p-methoxystyryl-6-methoxy-γ-pyrone.   Yangonic acid should be

$$MeO \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO_2H,$$
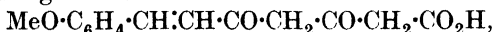
and yanganole the diketone $MeO \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$.

The structure of yanganole has been confirmed by synthesis.[70] p-Methoxycinnamoyl chloride with the sodium derivative of methyl acetoacetate furnished the diketonic ester,

$$MeO \cdot C_6H_4 \cdot CH{:}CH \cdot CO \cdot CH(CO \cdot CH_3) \cdot CO_2Me,$$
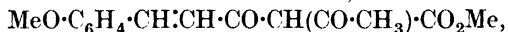
from which yanganole was obtained by hydrolysis.

An early investigation by C. Pomeranz [71] showed that methysticin was a neutral substance, $C_{15}H_{14}O_5$, which yielded protocatechuic acid on fusion with potassium hydroxide.   Aqueous alkali yielded methysticic acid, regarded as having the formula $C_{14}H_{12}O_5$.   This acid was oxidised to piperonylic acid.   It lost carbon dioxide above its melting point and was converted by boiling dilute acid or alkali into a ketone, methysticole, $C_{13}H_{12}O_3$.   Pomeranz concluded that methysticin was methyl methysticate with the structure

$$CH_2{<}^O_O{>}C_6H_3 \cdot CH{:}CH \cdot CH{:}CH \cdot CO \cdot CH_2 \cdot CO_2Me.$$

This formula was supported by E. Winzheimer,[72] who identified methysticole with piperonyleneacetone,

$$CH_2O_2{:}C_6H_3 \cdot CH{:}CH \cdot CH{:}CH \cdot CO \cdot CH_3,$$

prepared some years earlier from piperonylacraldehyde and acetone. This ketone is clearly to be expected on the above view of the structure of methysticin.

Nevertheless the observations that methysticin took up only two hydrogen atoms on catalytic hydrogenation [73] and that it was optically active [74] made it necessary to abandon Pomeranz's formula, and the presence of a γ-pyrone ring as in

$$CH_2O_2{:}C_6H_3 \cdot CH{:}CH \cdot CH{<}^{CH_2-CO}_{O \cdot C(OMe)}{\geqslant}CH$$
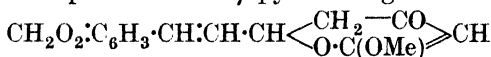
appeared likely.

It was found that the immediate product of the action of alkali upon methysticin was an isomeride, isomethysticin, which furnished methysticic acid on total hydrolysis.   Both isomethysticin and methysticic acid took up four atoms of hydrogen per molecule when subjected to catalytic hydrogenation, the latter being at the same time decarboxylated to tetrahydromethysticole.[75]

A substance, $allo$-methysticin, having the structure suggested by

[70] W. Borsche and C. Walter, *Ber.*, 1927, **60**, [*B*], 2112; *A.*, 1927, 1192.

[71] *Monatsh.*, 1888, **9**, 863; 1889, **10**, 783; *A.*, 1889, 278; 1890, 257.

[72] *Loc. cit.*

[73] H. Goebel, *Ber. deut. Pharm. Ges.*, 1922, **32**, 115; *A.*, 1922, i, 657.

[74] Y. Murayama and Shinozaki, *Chem. Zentr.*, 1925, ii, 2062.

[75] W. Borsche, *Ber.*, 1927, **60**, [*B*], 982; *A.*, 1927, 563.

Pomeranz was synthesised from piperic acid by condensing its chloride with methyl sodioacetoacetate and removing the acetyl group of the resulting ester,

$$CH_2O_2:C_6H_3 \cdot CH:CH \cdot CH:CH \cdot CO \cdot CH(CO \cdot CH_3) \cdot CO_2Me,$$

by means of ammonia. *allo*-Methysticin was of course not identical with methysticin, but neither was it identical with *iso*methysticin.[76]

*iso*Methysticin was found not to have the characteristic properties of a β-ketonic ester of reacting with ferric chloride and forming a copper derivative. As it dissolved in sodium carbonate, the facts were explained by the structure

$$CH_2O_2:C_6H_3 \cdot CH:CH \cdot CH:CH \cdot C(OMe):CH \cdot CO_2H$$

for *iso*methysticin. This was now confirmed by esterifying it by means of diazomethane and cautiously hydrolysing the product with acid, in such a manner that the enolic methoxyl group alone was affected. The product of this process was found, as expected, to have the properties of a β-ketonic ester and to be identical with the synthetic *allo*-methysticin.

All the facts are now accounted for by the α-pyrone structure

$$CH_2\!\!<^O_O\!\!>\!C_6H_3 \cdot CH:CH \cdot CH\!\!<^{CH_2 \cdot C(OMe)}_{O\text{------}CO}\!\!>\!CH$$ for methysticin, the

first action of alkali being to convert this lactone into the corresponding trebly unsaturated acid (*iso*methysticin).[77]

The substance ψ-methysticin occurring in kawa root has been found to be a partly hydrogenated methysticin, the latter being difficult to separate from its dihydro-derivative.

Kawa resin itself is composed largely of kawaic acid in the form of esters or pyrones.[78] The acid ($C_{14}H_{14}O_3$) easily loses carbon dioxide and distillation of the residue yields cinnamylideneacetone, whereas its tetrahydro-derivative passes smoothly on distillation into δ-phenylbutyl methyl ketone. The conclusion follows that kawaic acid is the analogue of *iso*methysticin, being hydrolysed by acids to methyl alcohol and γ-cinnamylideneacetoacetic acid or cinnamylideneacetone and carbon dioxide, but stable to alkalis. The formula $CHPh:CH \cdot CH:CH \cdot C(OMe):CH \cdot CO_2H$ is confirmed, as was that for *iso*methysticin, by partial demethylation of its methyl ester, the product being, as expected, methyl γ-cinnamylidene-acetoacetate.

It is probable that kawaic acid exists in the resin in the form of " kawain," an α-pyrone analogous to methysticin.

<div align="right">G. M. BENNETT.</div>

[76] W. Borsche, W. Rosenthal, and C. H. Meyer, *Ber.*, 1927, **60**, [*B*], 1135; *A.*, 1927, 664.

[77] W. Borsche, C. H. Meyer, and W. Peitzsch, *ibid.*, p. 2113; *A.*, 1927, 1192.

[78] W. Borsche and W. Peitzsch, *Ber.*, 1929, **62**, [*B*], 368; *A.*, 442; also W. Borsche and A. Roth, *Ber.*, 1921, **54**, [*B*], 2229; *A.*, 1921, i, 862.

PART III.—HETEROCYCLIC DIVISION.

Oxygen Ring Compounds.

SOME time ago it was observed that resacetophenone (2 : 4-dihydroxyacetophenone), on being heated with acetic anhydride and sodium acetate, was converted into 7-acetoxy-3-acetyl-2-methylchromone (I).[1] This reaction has been extended by R. Robinson and his collaborators during the past few years for the preparation of many naturally occurring products containing an oxygen ring. For the synthesis of flavones (2-phenylchromones) the general method of procedure has been to heat resacetophenone or phloracetophenone (2 : 4 : 6-trihydroxyacetophenone) with the anhydride and sodium salt of the appropriate substituted benzoic acid, and then to hydrolyse the acyloxy-compound which is first formed (acylation in the 3-position does not occur as a general rule). In this way, from resacetophenone, anisic anhydride and sodium anisate, there resulted 7-hydroxy-4'-methoxyflavone (II), which is probably identical with pratol from *Trifolium pratense*, and from

(I.)
$$AcO \overset{8}{\underset{7\ 6\ 5}{\bigcirc}} \overset{1}{\underset{4\ 3}{\bigcirc}} \overset{O}{\underset{CO}{}}\!\!\begin{array}{c} CMe \\ C\cdot COMe \end{array}$$

(II.)
$$HO \bigcirc\!\!\bigcirc \overset{O}{\underset{CO}{\underset{CH}{C}}}\!\!-\!\!\bigcirc OMe$$
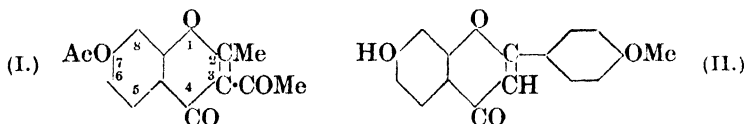
phloracetophenone, with the requisite reagents, chrysin (III; R = H) and acacetin (III; R = OMe) have been prepared.[2] 5 : 7-Dihydroxy-2' : 4'-dimethoxyflavone also has been synthesised by this method and subsequently converted, on demethylation, into 5 : 7 : 2' : 4'-tetrahydroxyflavone (IV), a compound which was

(III.)
$$HO \overset{O}{\underset{HO\ CO}{\bigcirc\!\!\bigcirc}}\!\!\overset{C}{\underset{CH}{}}\!\!-\!\!\bigcirc R$$

(IV.)
$$HO \overset{O\ \ HO}{\underset{HO\ CO}{\bigcirc\!\!\bigcirc}}\!\!\overset{C}{\underset{CH}{}}\!\!-\!\!\bigcirc OH$$
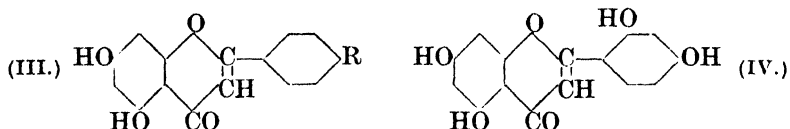
thought by W. R. Dunstan and T. A. Henry[3] to be lotoflavin, obtained by the hydrolysis of lotusin from *Lotus arabicus*, but apparently the natural product is not identical with the synthetical flavone.[4] It is interesting to note, however, that N. M. Cullinane,

(V.)
$$MeO \overset{}{\underset{MeO}{\bigcirc}}\!\!OH \quad MeO \overset{}{\underset{CO\cdot CH:CH}{}}\!\!-\!\!\bigcirc OMe$$

(VI.)
$$MeO \overset{O\ \ MeO}{\underset{MeO\ CO}{\bigcirc\!\!\bigcirc}}\!\!\overset{Br}{\underset{}{}}\!\!C:CH\!\!-\!\!\bigcirc OMe$$
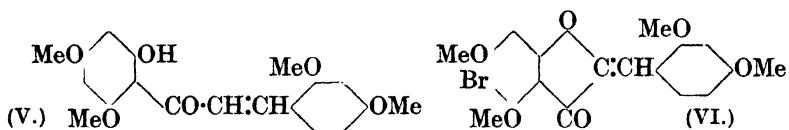
[1] Y. Tahara, *Ber.*, 1892, **25**, 1302; W. N. Nagai, *ibid.*, p. 1287; S. von Kostanecki and A. Rozycki, *Ber.*, 1901, **34**, 107.

[2] R. Robinson and K. Venkataraman, *J.*, 1926, 2344.

[3] *Phil. Trans.*, 1901, **194**, [B], 515.

[4] R. Robinson and K. Venkataraman, *J.*, 1929, 61.

J. Algar, and H. Ryan [5] have obtained 2-hydroxy-4 : 6 : 2′ : 4′-tetra-methoxybenzoylacetophenone by condensing phloracetophenone 4 : 6-dimethyl ether with methyl 2 : 4-dimethoxybenzoate in the presence of sodium at 150—160°, and have converted it by means of hydriodic acid into 5 : 7 : 2′ : 4′-tetrahydroxyflavone, which was thought to resemble natural lotoflavin, although complete identity was not established. Flavones can sometimes be obtained by the action of alkalis on the dibromides of o-hydroxyphenyl styryl ketones, and, with the structure of lotoflavin in mind, N. M. Cullinane and D. Philpott [6] have studied the possibility of preparing 5 : 7 : 2′ : 4′-tetrahydroxyflavone by this route from 2-hydroxy-4 : 6-dimethoxyphenyl 2 : 4-dimethoxystyryl ketone (V). Bromination, however, led to simultaneous nuclear substitution, and subsequent treatment with alkali gave a product which was probably 4-bromo-3 : 5 : 2′ : 4′-tetramethoxybenzylidenecoumaran-2-one (VI).

This acylation process has also been applied to gallacetophenone (2 : 3 : 4-trihydroxyacetophenone) [7] for the preparation of 7 : 8-dihydroxy-2-methylchromone and 7 : 8-dihydroxyflavone, both of which have been prepared previously by another method.[8] By extending the reaction to ω-methoxyresacetophenone and ω-methoxyphloracetophenone, derivatives of 3-methoxyflavone have been obtained [9]; in this way galangin monomethyl ether (VII; R = Me), occurring in galanga root, has been synthesised.[10] By first pre-

(VII.)
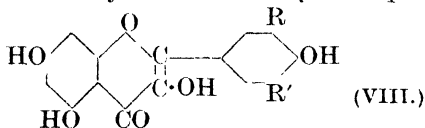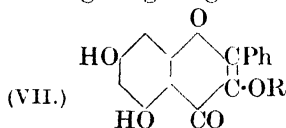
(VIII.)

paring the appropriate derivatives of 3-methoxyflavone and subsequently demethylating the products, the following naturally occurring flavonols (3-hydroxyflavones) have been synthesised : myricetin [11] (VIII ; R = R′ = OH), datiscetin [12] (IX ; R = H), kaempferol [13] (VIII ; R = R′ = H), fisetin [14] (X), quercetin [15] (VIII ; R = OH ; R′ = H), and morin [16] (IX ; R = OH). The

(IX.)

(X.)
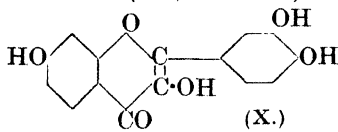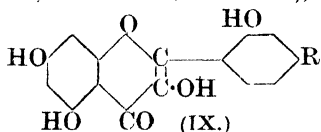
[5] *Proc. Roy. Dublin Soc.*, 1928, **19**, 77 ; *A.*, 703.   [6] *J.*, 1929, 1761.
[7] K. Venkataraman, *ibid.*, p. 2219.
[8] S. von Kostanecki and collaborators, *Ber.*, 1903, **36**, 2192, 4242.
[9] J. Allan and R. Robinson, *J.*, 1924, **125**, 2192.
[10] J. Kalff and R. Robinson, *J.*, 1925, **127**, 181.
[11] *Idem, loc. cit.*   [12] *Idem, ibid.*, p. 1968.
[13] R. Robinson and J. Shinoda, *ibid.*, p. 1973.
[14] J. Allan and R. Robinson, *J.*, 1926, 2334.   [15] *Idem, loc. cit.*
[16] R. Robinson and K. Venkataraman, *J.*, 1929, 61.

demethylation process has been avoided in the preparation of certain members of this class by employing ω-benzoyloxyphlor-acetophenone in the place of the ω-methoxy-derivative. Hydrolysis of the primary products then led directly to the flavanol, and the method has been used in the synthesis of galangin (VII; R = H), kaempferide (XI), and *iso*rhamnetin [17] (VIII; R = OMe; R' = H).
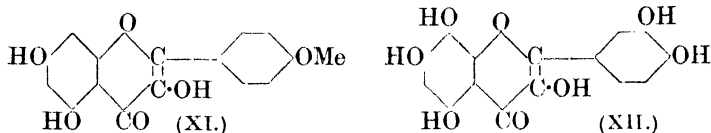
From ω-benzoyloxyphloracetophenone, *O*-benzylsyringic anhydride and sodium *O*-benzylsyringate, with subsequent hydrolysis of the product, 3 : 5 : 7 : 4'-tetrahydroxy-3' : 5'-dimethoxyflavone (VIII; R = R' = OMe) has been prepared.[18] This flavanol, which has been called syringetin, corresponds to the anthocyanidin, syringidin (malvidin), but it has not yet been obtained from natural sources. By a further application of these methods the structures of the two isomeric flavonols, gossypetin (XII) and quercetagetin (XIII), have been established.[19] Both of these interesting products are hydroxy-quercetins and contain a tetrahydroxybenzene nucleus. The former has been prepared by the interaction of 2 : 4-dihydroxy-ω : 3 : 6-trimethoxyacetophenone (XIV), veratric anhydride and
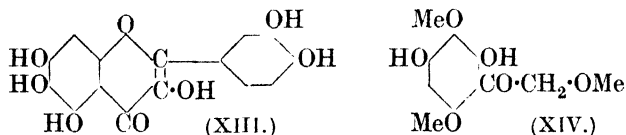
potassium veratrate, followed by hydrolysis and subsequent demethylation; the synthesis of quercetagetin was effected in a similar way from 2 : 6-dihydroxy-ω : 3 : 4-trimethoxyacetophenone (XV), a series of reactions which theoretically might also yield gossypetin. Some of the naturally occurring derivatives mentioned
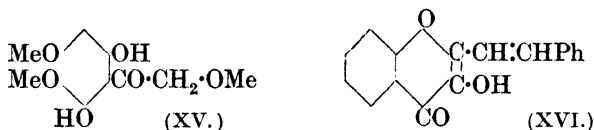
above have previously been prepared in other ways, but in many cases the structures assigned to the products have now for the first time received confirmation by synthesis.

[17] T. Heap and R. Robinson, *J.*, 1926, 2336.   [18] *Idem, ibid.*, 1929, 67.
[19] W. Baker, R. Nodzu, and R. Robinson, *ibid.*, p. 74.

By using ω-methoxyresacetophenone and ω-methoxyphloraceto-phenone, and extending this reaction with the aid of the anhydride and sodium salt of cinnamic acid, or a substituted cinnamic acid, it has been found possible to prepare derivatives of 2-styrylchromo-nol [20] (XVI), and a further development of the reaction has led to the preparation of *iso*flavones (3-phenylchromones). Although flavones are widespread in nature, so far only four members of the *iso*flavone group—prunetin, genistein (prunetol), irigenin, and ψ-baptigenin —have been recognised, and genistein has now been synthesised by W. Baker and R. Robinson.[21] 2 : 4 : 6-Trihydroxyphenyl *p*-methoxybenzyl ketone (XVII), on cinnamoylation and subsequent hydrolysis, gave 5 : 7-dihydroxy-4′-methoxy-2-styryl*iso*flavone [22] (XVIII; R = H), which was converted, on complete methylation,

(XVII.) HO

(XIX.)
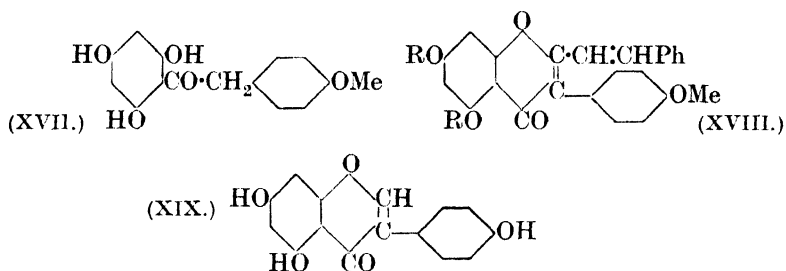
(XVIII.)

into 5 : 7 : 4′-trimethoxy-2-styryl*iso*flavone (XVIII; R = Me). This product was then oxidised by potassium permanganate in aqueous pyridine to 5 : 7 : 4′-trimethoxy*iso*flavone-2-carboxylic acid, which lost carbon dioxide above its melting point to give 5 : 7 : 4′-tri-methoxy*iso*flavone. The corresponding 5 : 7 : 4′-trihydroxy*iso*flav-one (XIX), obtained by demethylation, proved to be identical with genistein from *Genista tinctoria*.

An examination of the reactions of irigenin (XX; R = Me) has indicated that it is an *iso*flavone derivative,[23] which, on demethyl-ation, yields irigenol (XX; R = H). In order to confirm this structural formula, W. Baker and R. Robinson [24] heated 2 : 6-di-hydroxy-3 : 4-dimethoxyphenyl 3 : 4 : 5-trimethoxybenzyl ketone (XXI) with acetic anhydride and sodium acetate, and, after hydro-lysing the acetoxy-group in the product, obtained 5-hydroxy-6 : 7 : 3′ : 4′ : 5′-pentamethoxy-2-methyl*iso*flavone (XXII; R =Me).

[20] R. Robinson and J. Shinoda, *loc. cit.*
[21] *J.*, 1928, 3115.
[22] W. Baker and R. Robinson, *J.*, 1926, 2713.
[23] W. Baker, *J.*, 1928, 1022; *Ann. Reports*, 1928, **25**, 171.
[24] *J.*, 1929, 152.

(XX.)   (XXI.)   (XXII.)   (XXIII.)
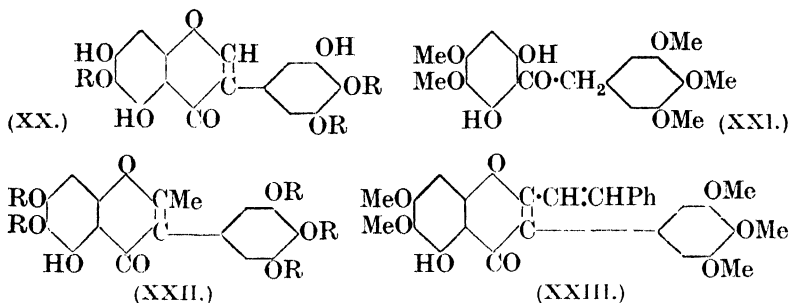
Theoretically, ring closure can take place here in two directions, but the course of the reaction is established by the fact that the product, when methylated and subsequently decomposed with alkali, yields 3 : 4 : 5-trimethoxyphenol   and   3 : 4 : 5-trimethoxyphenylacetic acid. This pentamethoxy-derivative, on demethylation, gave 5 : 6 : 7 : 3' : 4' : 5'-hexahydroxy-2-methyl*iso*flavone   (2-methylirigenol) (XXII ; R = H), the reactions and dyeing properties of which are so similar to those of irigenol as to leave no doubt concerning the structure of the latter substance. In an attempt to synthesise irigenin trimethyl ether, 5-hydroxy-6 : 7 : 3' : 4' : 5'-pentamethoxy-2-styryl*iso*flavone (XXIII) was prepared by the cinnamoylation of the ketone (XXI), but attempts to proceed along lines similar to those employed in the synthesis of genistein have not so far been successful.

It has now been shown[24a] that ψ-baptigenin, the glucoside of which is ψ-baptisin from the roots of *Baptisia tinctoria*, is a member of the *iso*flavone group with the structure (XXIV). On treatment with aqueous potassium hydroxide, it yielded formic acid and ψ-baptigenetin (XXV), which was found to be identical with the 2 : 4-dihydroxyphenyl 3 : 4-methylenedioxybenzyl ketone obtained by an application of the Hoesch reaction to resorcinol and 3 : 4-methylenedioxyphenylacetonitrile.

(XXIV.)   (XXV.)
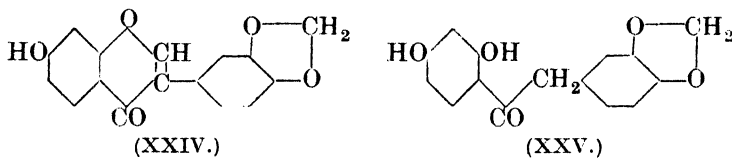
A new route for the synthesis of derivatives of 7-hydroxy*iso*-flavone has been introduced[25] by the preparation of 7-methoxy-

[24a] E. Späth and O. Schmidt, *Monatsh.*, 1929, **53** and **54**, 454; *A.*, 1458.
[25] W. Baker, A. Pollard, and R. Robinson, *J.*, 1929, 1468.

*iso*flavone (III) from the cyanohydrin of ω-*m*-methoxyphenoxy-acetophenone (I). The latter compound yielded, on cyclisation

$$\text{(I.)} \qquad \text{(II.)} \qquad \text{(III.)}$$
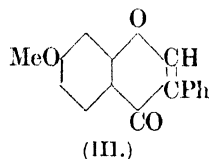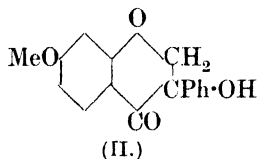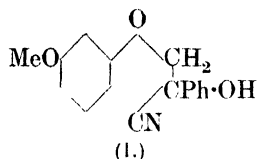
with zinc chloride and hydrogen chloride in ether, a ketimine hydrochloride, which, when hydrolysed, gave 3-hydroxy-7-methoxy-*iso*flavanone (II). 7-Methoxy*iso*flavone resulted readily on dehydration with cold concentrated sulphuric acid.

It is known that dehydration of catechin tetramethyl ether (IV) is accompanied by migration of the 3 : 4-dimethoxyphenyl group,[26] so that anhydrocatechin tetramethyl ether (V) contains the carbon skeleton of the *iso*flavone group of natural products. The genetic

$$\text{(IV.)} \qquad \text{(V.)}$$
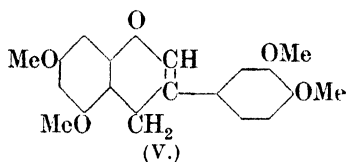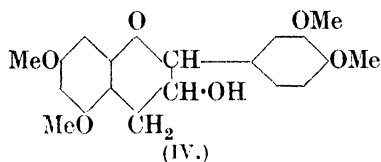
relationships existing between the several classes of natural products containing an oxygen ring constitute an interesting problem, and, with this in mind, W. Baker [27] has investigated the possibility of oxidising (V) to 5 : 7 : 3′ : 4′-tetramethoxy*iso*flavone (VI; R = Me), but this particular operation has not been successfully accomplished. This author has expressed the view, therefore, that the naturally occurring *iso*flavones are not derived from substances of the catechin type. Furthermore, it is significant that the *iso*flavone (VI; R = H), corresponding to the catechins, is unknown, as also are the catechins corresponding to the known *iso*flavones.

Investigations which have been carried out in Japan on the structures of two natural products, matteucinol and carthamin, are of considerable interest. S. Fujise [28] has shown that matteucinol, a product obtained from *Matteucia orientalis*, is a flavanone of the constitution (VII; R = OMe). Thus it was found to give the colour reaction of this class with magnesium and hydrochloric acid, to be phenolic in character, and to yield a monomethyl ether with diazomethane. On fusion with potash, *p*-methoxycinnamic acid

[26] K. Freudenberg and collaborators, *Annalen*, 1925, **441**, 157; 1925, **446**, 87; *A*., 1925, i, 419; 1926, 73.

[27] *J*., 1929, 1593.

[28] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, 111.

and 2 : 4-dimethylphloroglucinol (VIII) were obtained. Matteu-
cinol was synthesised by condensing (VIII) with p-methoxycinnam-
oyl chloride in nitrobenzene in the presence of aluminium chloride,

RO ⌂ CH   OR   HO ⌂ CH–⟨⟩R   HO ⌂ OH
RO   C—⟨⟩OR   Me   CH₂   Me
RO   CO   HO   CO   HO
(VI.)   (VII.)   (VIII.)
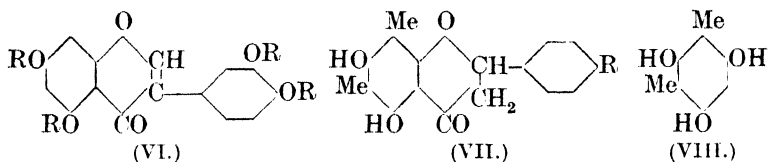
a reaction already used for preparing flavanones.[29]   A second pro-
duct, which appears to be (VII; R = H), has also been isolated
from the same source. These substances are of especial interest
since they contain a methylated benzene nucleus, which is very
rare among natural products. The investigation into the structure
of carthamin, a red dye from safflower, has been carried out by Miss
C. Kuroda.[30]   Cold dilute hydrochloric acid converts it into the

HO   O   RO
HO ⌂ CH—⟨⟩OH   O ⌂ OH   CH—⟨⟩OH
HO   CO   (IX.)   HO   C   (X.)
CH₂   OH

RO   MeO
HO ⌂ OH   CH—⟨⟩OH   MeO ⌂ OMe   CH—⟨⟩OMe
HO   CO   (XI.)   MeO   CO   (XII.)
CH
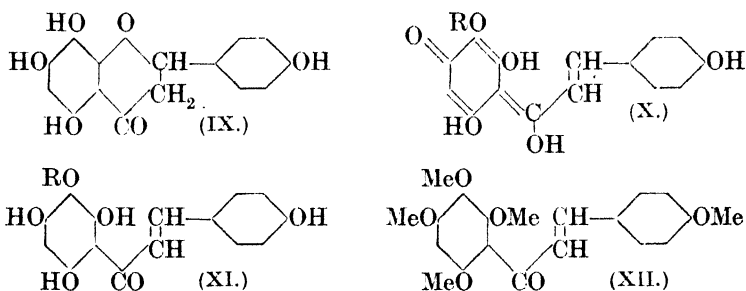
isomeric isocarthamin. Hydrolysis with dilute mineral acids gives
a molecule of glucose, and, if dilute phosphoric acid is used, the
glucose-free carthamidin, $C_{15}H_{12}O_6$, together with isocarthamidin,
can be isolated. As a result of a comparison of the reactions of
derivatives of these substances with those of known chalkones and
flavanones it is suggested that carthamidin is 5 : 7 : 8 : 4'-tetra-
hydroxyflavanone (IX) and isocarthamidin the 5 : 6 : 7 : 4'-tetra-
hydroxy analogue, whilst carthamin is believed to be the chalkone
(X; R = glucose residue) and isocarthamin the isomeric compound
(XI). These views are confirmed by the preparation from cartham-
idin of 2 : 3 : 4 : 6-tetramethoxyphenyl p-methoxystyryl ketone
(XII), which was identified by synthesis.

During the course of other work with oxygen ring compounds,
but not directly connected with natural products, it has been

[29] Compare Ann. Reports, 1928, **25**, 169.
[30] Proc. Imp. Acad. Tokyo, 1929, **5**, 32, 82, 86; A., 430, 703.

observed that the isomeric benzopyrylium salts (I and II) condense with 2-naphthol-1-aldehyde in the presence of hydrogen chloride and that, when the resulting salts are hydrolysed, the corresponding isomeric 3- and 3'-substituted benzo-β-naphtha*spiro*pyrans (III) are respectively formed. These differ from one another in the fact that the 3-substituted products give coloured solutions in hot inert solvents, but the 3'-substituted compounds do not show this phenomenon.[31] This reaction has accordingly been used by I. M. Heilbron and F. Irving [32] to determine the reactive group under various conditions in ketones of the type $CH_3 \cdot CO \cdot CH_2R$. Thus by condensation with salicylaldehyde, the isomeric products (IV) and
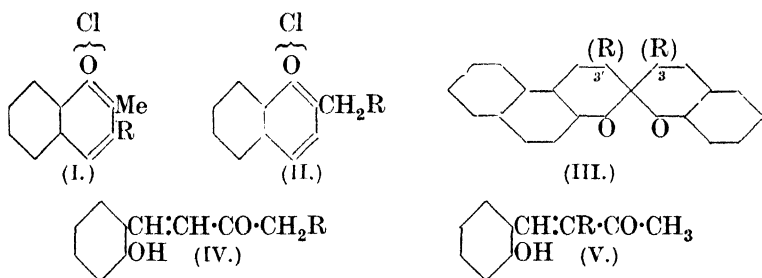
(V) can result, and these, on further treatment with hydrogen chloride and 2-naphthol-1-aldehyde, yield, on subsequent hydrolysis, *spiro*pyrans which can be readily distinguished.

The reaction between resacetophenone and ethyl ethoxymethyleneacetoacetate in alcoholic sodium ethoxide has been found to yield 7-hydroxy-3 : 6-diacetylcoumarin,[33] and the process constitutes a new method for the preparation of a number of coumarins, since it can be extended to derivatives of resorcinol in conjunction with the above ester or ethyl ethoxymethylenemalonate.[34] It has also been observed [35] that ethyl phenylcyanopyruvate and resorcinol react together in glacial acetic acid, in the presence of hydrogen chloride and zinc chloride, not in accordance with the normal Hoesch reaction, but to give ethyl 7-hydroxy-3-phenylcoumarin-4-carboxylate. A similar reaction takes place with orcinol and phloroglucinol.[36]

[31] R. Dickinson and I. M. Heilbron, *J.*, 1927, 1699.

[32] *J.*, 1929, 936.

[33] R. Weiss and E. Merksammer, *Monatsh.*, 1928, **50**, 115; *A.*, 73.

[34] R. Weiss and A. Kratz, *ibid.*, 1929, **51**, 386; *A.*, 821.

[35] W. Borsche and J. Niemann, *Ber.*, 1929, **62**, [*B*], 2043; *A.*, 1309.

[36] Compare also A. Sonn, *ibid.*, 1918, **51**, 821, 1829; *A.*, 1918, i, 401; 1919, i, 192.

Selenium Ring Compounds.

Following upon the preparation of *cyclo*telluropentane [37] and selenophen,[38] it is interesting to note the synthesis of *cyclo*selenobutane (tetrahydroselenophen) (I; $n = 2$) by G. T. Morgan and F. H. Burstall [39] from the interaction of tetramethylene dibromide with sodium selenide. An alternative method is to act upon tetramethylene dibromide with potassium selenocyanate with the formation of tetramethylene diselenocyanate (II), hydrolysis of which by alcoholic alkali, together with aerial oxidation, gives *cyclo*tetramethylene diselenide (III). The latter loses selenium, on heating, and yields *cyclo*selenobutane. *cyclo*Selenobutane, containing bivalent selenium, combines additively with a variety of substances.

$$(CH_2)_n\!\!<\!\!\begin{array}{c}CH_2\\CH_2\end{array}\!\!>\!\!Se \qquad \begin{array}{c}CH_2 \cdot CH_2 \cdot Se \cdot CN\\CH_2 \cdot CH_2 \cdot Se \cdot CN\end{array} \qquad \begin{array}{c}CH_2 \cdot CH_2 \cdot Se\\CH_2 \cdot CH_2 \cdot Se\end{array}$$

(I.)   (II.)   (III.)
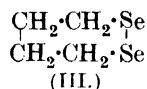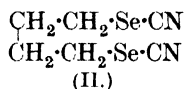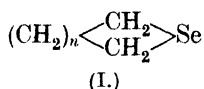
The same authors [40] have also prepared *cyclo*selenopentane (I; $n = 3$) by an application of both these methods to pentamethylene dibromide. *cyclo*Selenopentane also readily forms addition products, but these are, in general, rather less stable than the corresponding derivatives of *cyclo*selenobutane.

Indole Derivatives.

Further investigations have been made during the past year into the various types of addition reaction into which indoles and indolenines can enter. It has been observed by S. G. P. Plant [41] that the 8-acyldihydropentindoles (I; $n = 1$; $R = Ac$, Bz, or CO_2Et), under certain conditions of nitration, not only give mononitro-substitution products but also take up the elements of nitric acid, presumably at the double linkage in the indole skeleton, with the formation of compounds of the type (II). Of the analogous 9-acyltetrahydrocarbazoles (I; $n = 2$; $R = Ac$, Bz, CO_2Et, or $Ph \cdot CH_2 \cdot CO$), only the benzoyl compound gives a substance of this

(I.)   (II.)   (III.)
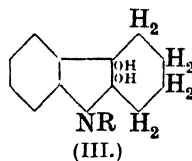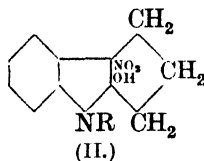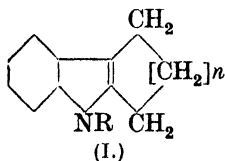
nature, the remaining acyl derivatives, under similar conditions,

[37] G. T. Morgan and H. Burgess, *J.*, 1928, 321; *Ann. Reports*, 1928, **25**, 196.

[38] H. V. A. Briscoe and J. B. Peel, *J.*, 1928, 1741; *Ann. Reports*, 1928, **25**, 174.

[39] *J.*, 1929, 1096.   [40] *Ibid.*, p. 2197.   [41] *Ibid.*, p. 2493.

yielding products (III; $R = Ac$, CO_2Et, or $Ph \cdot CH_2 \cdot CO$) which have resulted from oxidation at the double linkage and the consequent addition of two hydroxyl groups.[42] These several addition products undergo many interesting reactions under various conditions. In some instances, the action of alkali on the compound (II) leads to the rupture of the indole system and the formation of benzene derivatives of the type (IV). H. Leuchs, A. Heller, and A. Hoffmann[43] have found that, with certain limitations, the addition reactions observed between acid anhydrides and indeno-ψ-indolines[44] can be applied to the simpler indolenines. Thus 3 : 3-dimethylindolenine (V) gives 2-acetoxy-1-acetyl-3 : 3-dimethyl-2 : 3-dihydroindole (VI) on treatment with acetic anhydride and

$$\text{(IV.)} \qquad \text{(V.)} \qquad \text{(VI.)}$$

Structures: (IV.) benzene ring with $CO \cdot [CH_2]_n \cdot CO_2H$ and NHR; (V.) with CMe_2, CH, N; (VI.) with CMe_2, $CH \cdot OAc$, NAc.
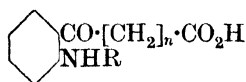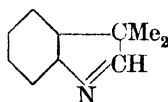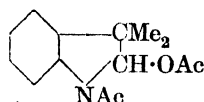
sodium acetate at 100°, and the analogous 2-benzoyloxy-1-benzoyl derivative can be similarly prepared, but it was not possible to add phthalic anhydride. In the case of 3 : 3-dibenzyl-2-methylindolenine (VII), similar experimental conditions resulted, not in the addition of acetic anhydride or benzoic anhydride, but in the acylation of the tautomeric form of (VII) with the formation of 1-acetyl- or

$$\text{(VII.)} \qquad \text{(VIII.)} \qquad \text{(IX.)}$$

Structures: (VII.) with $C(CH_2Ph)_2$, CMe, N; (VIII.) with $C(CH_2Ph)_2$, $C{:}CH_2$, NR; (IX.) with CMe_2, $C(OH) \cdot Ph$, NBz.
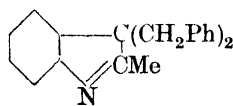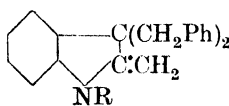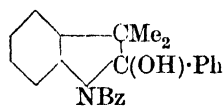
1-benzoyl-3 : 3-dibenzyl-2-methylene-2 : 3-dihydroindole (VIII; $R =$ Ac or Bz). 2-Phenyl-3 : 3-dimethylindolenine does not combine additively with acetic anhydride, but, on treatment with benzoyl chloride and sodium carbonate, it gives 2-hydroxy-1-benzoyl-2-phenyl-3 : 3-dimethyl-2 : 3-dihydroindole (IX).

Some time ago R. Pummerer[45] claimed to have prepared isatin-2-anil in two tautomeric modifications (X and XI; $R = H$), but this was disputed by H. Rupe and K. Apotheker.[46] It has now been shown, however, by R. K. Callow and E. Hope[47] that the arguments of the latter authors are unsound, and Pummerer's views have been confirmed by the preparation of both isomeric benzoyl derivatives (X and XI; $R =$ Bz) from isatin-2-anil by benzoylation

[42] W. H. Perkin and S. G. P. Plant, *J.*, 1923, **123**, 676.
[43] *Ber.*, 1929, **62**, [*B*], 871; *A.*, 704.   [44] See *Ann. Reports*, 1928, **25**, 175.
[45] *Ber.*, 1911, **44**, 338, 810; *A.*, 1911, i, 231, 399.
[46] *Helv. Chim. Acta*, 1926, **9**, 1049; *A.*, 1927, 61.   [47] *J.*, 1929, 1191.

under the appropriate conditions. It has been recorded by J. Martinet and A. Dansette [48] that ethyl 1-phenyl-4 : 5-benzodiox-

indole-3-carboxylate (XII), obtained from the interaction of N-phenyl-β-naphthylamine and ethyl mesoxalate, can be converted by alkalis under various conditions into 1-phenyl-4 : 5-benzodioxindole (XIII), 1-phenyl-4 : 5-benzoisatin (XIV), or the naphthacridine-

carboxylic acid (XV). The conversion of derivatives of 1-phenyl-isatin into the corresponding acridinecarboxylic acids has previously been observed.[49]
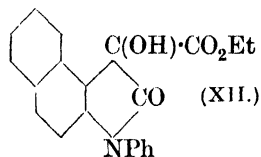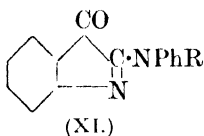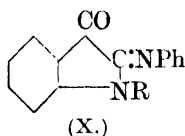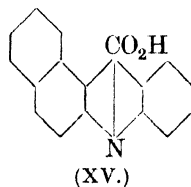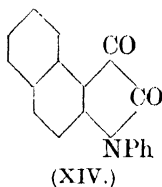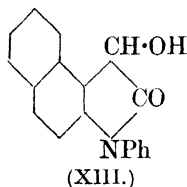
A series of reactions, analogous to some already used in the preparation of carboline derivatives,[50] has been employed as an additional method for the synthesis of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline [51] (XVII). The phenylhydrazone of ethyl δ-phthalimido-α-ketovalerate, obtained by the action of benzenediazonium chloride on ethyl δ-phthalimido-α-acetylvalerate in alkaline-alcoholic solution, gave, by the usual Fischer reaction, ethyl 3-β-phthalimido-ethylindole-2-carboxylate (XVI), from which the final product was secured by heating first with hydrazine hydrate in alcohol and then with hydrochloric acid. The preparation of tetrahydroharman (XVIII) by the action of paraldehyde on 3-β-aminoethylindole has also been described.[52]
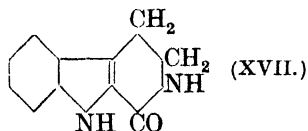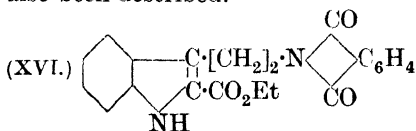
[48] *Bull. Soc. chim.*, 1929, [iv], **45**, 101; *A.*, 452.

[49] P. Friedländer and K. Kunz, *Ber.*, 1922, **55**, [B], 1597; *A.*, 1922, i, 765; R. Stollé, *J. pr. Chem.*, 1922, [ii], **105**, 137; *A.*, 1923, i, 1125.

[50] R. H. F. Manske, W. H. Perkin, and R. Robinson, *J.*, 1927, 1.

[51] S. Keimatsu, S. Sugasawa, and G. Kasuya, *J. Pharm. Soc. Japan*, 1928, No. 558, 762; *A.*, 195.

[52] G. Tatsui, *ibid.*, No. 555, 453; *A.*, 74.

E. W. McClelland [53] has prepared thionaphthindole (XIX) by the interaction of o-thiolacetophenone with phenylhydrazine in glacial acetic acid, a reaction which proceeds readily and undoubtedly involves first an ordinary Fischer synthesis to give (XX), followed

(XVIII.)   (XIX.)   (XX.)

(XXI.)   (XXII.)
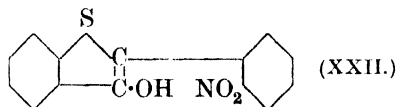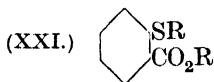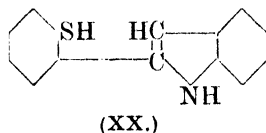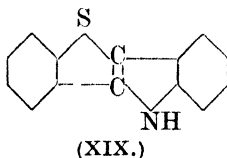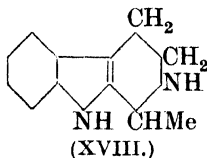
by oxidation. The constitution assigned to the product was confirmed by synthesising it from o-thiolbenzoic acid, which was converted first into the ester (XXI; $R = o\text{-}NO_2 \cdot C_6H_4 \cdot CH_2$), then, by alcoholic potassium ethoxide, into (XXII), and finally, by reduction with zinc dust and acetic acid, into thionaphthindole. The product showed the general reactions of indole derivatives.

Quinoline Derivatives.

Although the amount of published work dealing with the cyanine dyes has been considerably less this year than during the previous year,[54] some observations of considerable interest have been made. It is well known that 1-methylbenzthiazole (I) can be used for the production of several different types of cyanine dye, and Miss F. M. Hamer [55] has now extended our knowledge of some of these classes by preparing the corresponding dyes from the two methylnaphthathiazoles (II and III) and comparing them with their simpler analogues.

(I.)   (II.)   (III.)
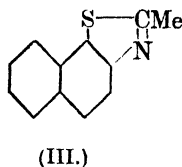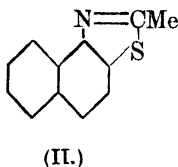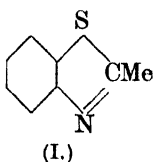
All the various classes of carbocyanine dyes contain two heterocyclic nuclei united by the carbon chain $:CH \cdot CH:CH\cdot$, but very little is known of derivatives in which one or more of the hydrogen atoms attached to this chain are replaced by other groups. The neocyanines probably provide examples of this type,[56] and Miss

[53] *J.*, 1929, 1588.　　　　　　　[54] See *Ann. Reports*, 1928, **25**, 179.
[55] *J.*, 1929, 2598.　　　　　　　[56] Miss F. M. Hamer, *J.*, 1928, 1472.

F. M. Hamer [57] has now succeeded in preparing three methylthio-carbocyanines of the structure (IV) by the action of ethyl ortho-acetate in the presence of pyridine on the corresponding 1-methyl-benzthiazole alkylhalides. This is an application of Miss Hamer's well-known method of preparing the carbocyanines with the aid of ethyl orthoformate and pyridine, but it has been found that the carbocyanine syntheses in general cannot be satisfactorily extended in this way. The substituted thiocarbocyanines, like the parent compounds, are photographic sensitisers.
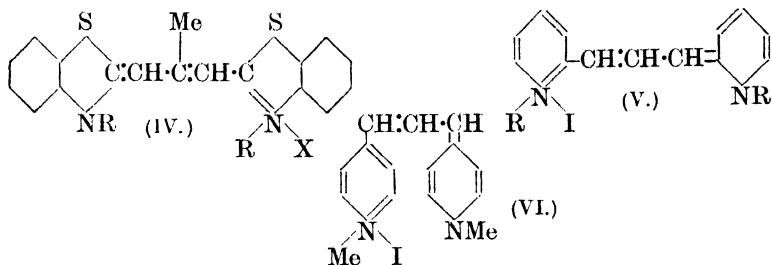
Although many classes of cyanine and carbocyanine dyes derived from quinoline and other binuclear heterocyclic compounds have been described, very little is known concerning the simpler, analogous derivatives of pyridine and other monocyclic systems. E. Rosen-hauer and F. Barlet,[58] however, have now prepared the 2 : 2'-carbo-pyridinecyanines (V) from α-picoline alkyliodide by the action of chloroform and potash in alcoholic solution under the correct con-ditions, and a similar procedure with γ-picoline methiodide yielded the 4 : 4'-carbopyridinecyanine (VI). These dyes, like the corre-sponding quinoline derivatives, are photographic sensitisers.

Further studies [59] into the formation of stereoisomerides which owe their existence to the *cis*- and *trans*-unions of two ring systems [60] have led to an investigation of the action of sodium amalgam upon 5-keto-2 : 3 : 5 : 6-tetrahydro-α-quinindene (VII) in boiling alcohol. The reaction resulted only in the addition of two atoms of hydrogen, and, although two stereoisomeric forms (called A and B) of 5-keto-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene (VIII) were obtained,
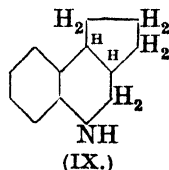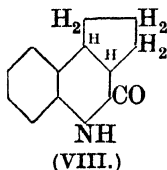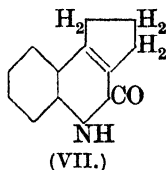
[57] *J.*, 1928, 3160.   [58] *Ber.*, 1929, **62**, [*B*], 2724.
[59] B. K. Blount, W. H. Perkin, and S. G. P. Plant, *J.*, 1929, 1975.
[60] See *Ann. Reports*, 1928, **25**, 183.

the (B) modification greatly preponderated. The interesting observation was made that further reduction of the mixture of these two stereoisomerides with sodium and boiling alcohol yielded a single modification only of $2 : 3 : 4 : 5 : 6 : 13$-hexahydro-α-quinindene (IX), a fact which can be explained if the reaction is assumed to take the following course :
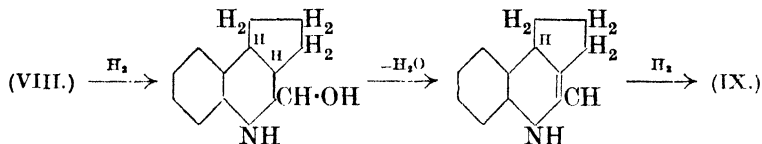
Furthermore it has been found that 12-keto-$2 : 3 : 5 : 12$-tetrahydro-β-quinindene (X) is fully reduced by sodium amalgam in boiling alcoholic solution to give both stereoisomeric forms (A and B) of $2 : 3 : 4 : 5 : 12 : 13$-hexahydro-β-quinindene (XI), but the (B) form constitutes by far the main part of the product, whereas, during the reduction of $2 : 3$-dihydro-β-quinindene (XII) with tin and alcoholic hydrochloric acid, the amounts of (A) and (B) produced are approximately in the ratio of $1 : 3$. It has become apparent that the amounts of the two stereoisomerides formed in these and the analogous reactions previously investigated do not depend mainly upon the relative strains in the two configurations, but are determined by the collective effect of several factors.
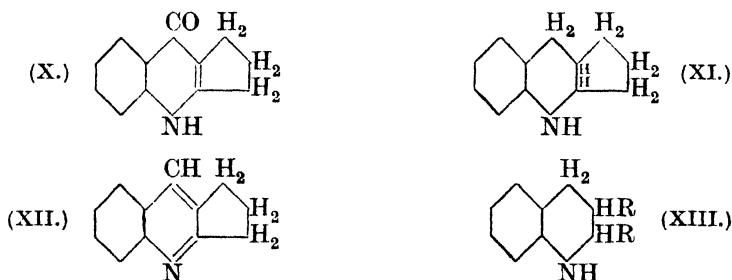
It has also been observed [61] that $2 : 3$-dimethyl- and $2 : 3$-diphenyl-$1 : 2 : 3 : 4$-tetrahydroquinoline (XIII; $R = Me$ or Ph) are each produced in two stereoisomeric forms during the reduction of the corresponding disubstituted quinolines, the relative amounts of the different modifications varying considerably with the nature of the reducing agent used.

[61] S. G. P. Plant and R. J. Rosser, *J.*, 1929, 1861.

Systems with Two (or More) Hetero-atoms.

Once again many papers have appeared during the year dealing with compounds belonging to the large number of different classes which contain more than one hetero-atom in the cyclic nucleus. It is impossible in this Report to deal with more than a few interesting points, and these involve, as a general rule, applications of reactions which are already well known in the simpler series.

Several instances of tautomerism have been recorded. For example, it has been observed [62] that the 2-amino-oxazolines and the 2-aminothiazolines exist in the two modifications (I and II; R = H), and, on interaction with phenylthiocarbimide, for example,

$$
\begin{array}{cc}
\text{(I.)} & \text{(II.)} \\
\underset{(S)}{\overset{\displaystyle\begin{array}{c}\text{CH}_2\text{—N}\\ \text{R'CH} \quad \text{C·NHR}\\ \diagdown\diagup\\ \text{O}\end{array}}{}} &
\underset{(S)}{\overset{\displaystyle\begin{array}{c}\text{CH}_2\text{—NR}\\ \text{R'CH} \quad \text{C:NH}\\ \diagdown\diagup\\ \text{O}\end{array}}{}}
\end{array}
$$

they give rise to two different products (I and II; R = ·CS·NHPh) according to the temperature. In the *iso*oxazole series, the tautomeric change (III) ⇌ (IV) has been studied by the preparation

$$
\begin{array}{cc}
\text{(III.)} & \text{(IV.)} \\
\overset{\displaystyle\begin{array}{c}\text{NH}_2\text{·C}\text{——C}\text{Ar}\\ \text{HO·C} \quad \text{N}\\ \diagdown\diagup\\ \text{O}\end{array}}{} &
\overset{\displaystyle\begin{array}{c}\text{NH:C}\text{——C}\text{Ar}\\ \text{HO·CH} \quad \text{N}\\ \diagdown\diagup\\ \text{O}\end{array}}{}
\end{array}
$$

of a number of derivatives of both forms.[63]   There is also evidence that the fully substituted triphenyl*iso*oxazolium hydroxides (V) tautomerise to the corresponding ψ-bases (VI). The latter undergo loss of water to give anhydro-bases which apparently have the

$$
\begin{array}{ccc}
\text{(V.)} & \text{(VI.)} & \text{(VII.)} \\
\underset{\text{O}}{\overset{\displaystyle\begin{array}{c}\text{PhC——CPh}\\ \text{PhC} \quad \text{N}\diagdown\!\begin{array}{c}\text{CH}_2\text{R}\\ \text{OH}\end{array}\\ \diagdown\diagup\end{array}}{}} &
\underset{\text{O}}{\overset{\displaystyle\begin{array}{c}\text{PhC====CPh}\\ \text{PhC·OH} \quad \text{N·CH}_2\text{R}\\ \diagdown\diagup\end{array}}{}} &
\overset{\displaystyle\begin{array}{c}\text{Ph}\diagdown\\ \quad\quad\text{C:CPh·N:CHR}\\ \text{Bz}\diagup\end{array}}{}
\end{array}
$$
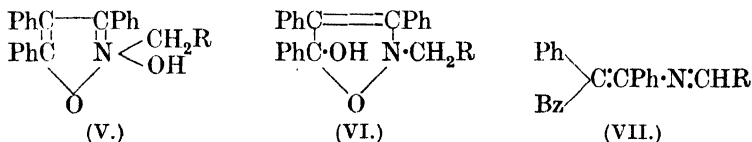
structure (VII).[64]   Some interesting observations of an analogous character have been made [65] during a study of certain well-known methods for the preparation of pyrazolines. The action of aliphatic diazo-compounds on ethylenic substances gives first a derivative, containing ⁻N═N⁻ in the ring, which then isomerises to the pyr-

[62] E. Fromm, *Annalen*, 1926, **447**, 259; *A.*, 1926, 716; E. Fromm and R. Kapeller-Adler, *ibid.*, 1928, **467**, 240; *A.*, 199.

[63] G. Ponzio and M. Torres, *Gazzetta*, 1929, **59**, 461; *A.*, 1316.

[64] E. P. Kohler and A. H. Blatt, *J. Amer. Chem. Soc.*, 1928, **50**, 1217; *A.*, 1928, 652; E. P. Kohler and N. K. Richtmyer, *ibid.*, p. 3092; *A.*, 77.

[65] K. von Auwers and E. Cauer, *Annalen*, 1929, **470**, 284; *A.*, 1080.

azoline. If the ethylenic compound is an $\alpha\beta$-unsaturated ester, the intermediate substance (VIII) (the nitrogen uniting with the α-carbon atom) might undergo isomeric change in two different directions to give (IX) or (X). The application of this reaction to a number

$$\begin{array}{ccc} \text{RCH—CH·CO}_2\text{R}' & \text{RCH—CH·CO}_2\text{R}' & \text{RCH—C·CO}_2\text{R}' \\ \text{XCH} \quad \text{N} & \text{XC} \quad \text{NH} & \text{XCH} \quad \text{N} \\ \diagdown\!\!\diagup & \diagdown\!\!\diagup & \diagdown\!\!\diagup \\ \text{N} & \text{N} & \text{NH} \\ \text{(VIII.)} & \text{(IX.)} & \text{(X.)} \end{array}$$
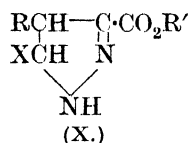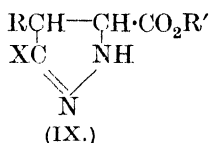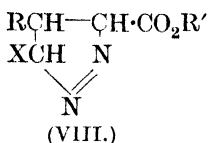
of esters, with diazomethane and diazoethane, yielded exclusively products of the type (X), but the isomeric pyrazolines of type (IX) can be obtained by the action of hydrazine on β-acylacrylic esters. It seems, therefore, that the isomerisation of (VIII) proceeds in that direction which leads to a conjugated system of double linkages. When the unsaturated compound is an unsymmetrical dicarboxylic ester, the number of possibilities is increased, and the action of diazomethane on methyl citraconate has yielded, together with other substances, a product (XI) in which the type (VIII) appears to have been realised, since it does not contain a secondary nitrogen atom, and can be converted by hydrogen chloride into the normal type through the migration of a hydrogen atom. The type (VIII) seems also to find a stable existence in the product of the inter-action of diazomethane and methyl dimethylmaleate.

$$\begin{array}{cc} \text{MeO}_2\text{C·CH—CMe·CO}_2\text{Me} & \text{PhC—N} \\ \text{(XI.)} \qquad \text{CH}_2 \quad \text{N} & \text{CH} \quad \text{C·NH·NHPh} \quad \text{(XII.)} \\ \diagdown\!\!\diagup & \diagdown\!\!\diagup \\ \text{N} & \text{S} \end{array}$$
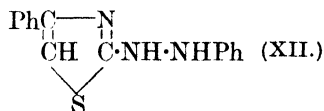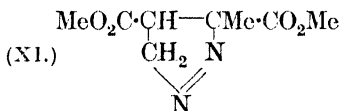
Amongst other types of migration reactions some examples of the benzidine rearrangement have been described. For instance, 2-phenylhydrazino-4-phenylthiazole (XII), when treated with boiling dilute hydrochloric acid, gives 2-amino-4-phenyl-5-p-amino-phenylthiazole (XIII),[66] and the reaction has been extended to a considerable number of closely related compounds substituted in

$$\begin{array}{cc} \qquad\qquad \text{PhC—N} & \text{NHPh·NH·C—CMe} \\ \text{(XIII.) NH}_2\!\!\bigcirc\!\!-\!\!\text{C} \quad \text{C·NH}_2 & \text{PhC} \quad \text{N} \quad \text{(XIV.)} \\ \qquad\qquad \diagdown\!\!\diagup & \diagdown\!\!\diagup \\ \qquad\qquad \text{S} & \text{O} \end{array}$$
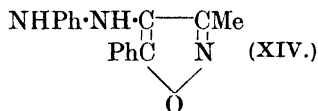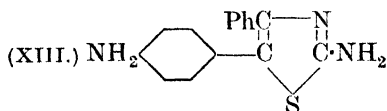
the phenyl groups. Furthermore, it has been observed that 4-phenyl-hydrazino-5-phenyl-3-methyl*iso*oxazole (XIV) is converted by heating with N-hydrochloric acid into a mixture of 5-anilino-5-phenyl-

[66] P. K. Bose, *J. Indian Chem. Soc.*, 1927, **4**, 331; *A.*, 1928, 188; P. K. Bose and B. K. Sen, *ibid.*, 1928, **5**, 643; *A.*, 79; B. C. Das-Gupta and P. K. Bose, *ibid.*, 1929, **6**, 495; *A.*, 1317.

3-methyl*iso*oxazol-4-one (XV) and 4-imino-5-phenyl-5-*o*-amino-phenyl-3-methyl*iso*oxazoline (XVI). The formation of the latter product is due to an *o*-benzidine rearrangement.[67]

$$
\text{(XV.)} \quad \underset{\underset{O}{\diagdown\diagup}}{\overset{\overset{\displaystyle CO-CMe}{|\quad\quad|}}{NHPh{\cdot}CPh\ N}}
\qquad\qquad
\text{(XVI.)} \quad
$$

NH:C̤——CMe
——CPh N
NH₂
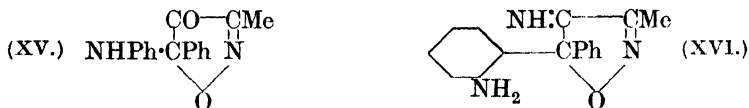
Two interesting ring transformations are involved in the reactions of certain benz*iso*oxazole derivatives.[68] 5-Nitro-2-acetamidobenz-*iso*oxazole (XVII), on warming with 2*N*-sodium hydroxide, gives 3-4'-nitro-2'-hydroxyphenyl-5-methyl-1 : 2 : 4-oxdiazole (XVIII),

$$
\text{NO}_2 \quad \overset{C{\cdot}NH{\cdot}CO{\cdot}CH_3}{N} \quad (XVII.)
\qquad\qquad
\text{NO}_2 \quad \overset{C——N}{\underset{OH\ \ N\diagup CMe}{}} \quad (XVIII.)\ O
$$
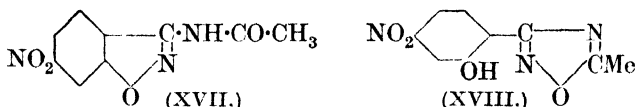
which involves fission of the *iso*oxazole ring and subsequent inter-action of the oximino- and the acetamido-group. When 5-nitro-2-hydroxybenz*iso*oxazole is treated with acetic acid, it undergoes fission to 4-nitro-2-hydroxybenzacetylhydroxamic acid (XIX), which, with methyl-alcoholic potash, is converted into 5-nitrobenz-oxazol-1-one (XX), a change which involves first hydrolysis to the free hydroxamic acid and then a Beckmann rearrangement.

$$
\text{(XIX.)} \quad \text{NO}_2 \quad \overset{C{\cdot}OH}{\underset{OH\ \ N{\cdot}OAc}{}}
\qquad\qquad
\text{NO}_2 \quad \overset{NH}{\underset{O}{CO}} \quad \text{(XX.)}
$$
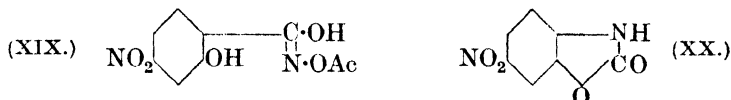
The thermal decomposition of a large number of alkylhalides of heterocyclic nitrogen compounds which also contain other alkyl groups attached to the hetero-nucleus has been studied in order to determine the relative tenacities of the various hydrocarbon radicals, not only when two are both attached to nitrogen atoms, but also when they are bound to differing atoms, *e.g.*, carbon and nitrogen.[69] The systems investigated include, amongst others, the quaternary indazolium salts (XXI), the iodides of *NN'*-dialkylbenziminazoles

$$
\text{(XXI.)} \quad \left[C_6H_4{<}^{CH}_{NR'}{>}NR \right] X
\qquad\qquad
\left[C_6H_4{<}^{NR}_{NR'}{>}CH \right] I \ \text{(XXII.)}
$$

$$
\text{(XXIII.)} \quad \left[\overset{Me_2C——CMe}{\underset{\underset{NR}{MeC\diagdown\ \ N}}{}} \right] I
\qquad\qquad
\left[\overset{CH—CMe}{\underset{\underset{NPh}{R'S{\cdot}C\diagdown\ \ NR}}{}} \right] I \ \text{(XXIV.)}
$$
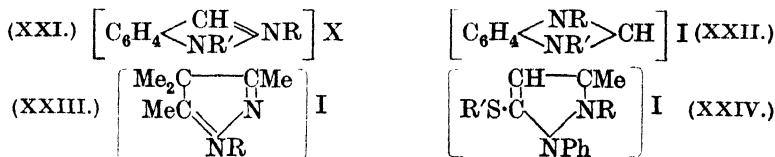
⁶⁷ G. Wittig, H. Kleiner, and J. Conrad, *Annalen*, 1929, **469,** 1; *A.*, 456.

⁶⁸ H. Lindemann and H. Cissée, *ibid.*, p. 44; *A.*, 456.

⁶⁹ K. von Auwers and his collaborators, *Ber.*, 1925, **58,** [*B*], 1360; *A.*, 1925, i, 1100; *Ber.*, 1928, **61,** [*B*], 100, 2411; *A.*, 1928, 306; 1929, 75; *Annalen,* 1929, **469,** 82; 472, 287; *A.*, 454, 1081.

(XXII), substituted pyrazole alkyliodides (XXIII), and thiopyrine ψ-alkyliodides (XXIV), and the results show that, as a general rule, the tenacity with which the simple alkyl groups are attached to two nitrogen atoms increases with the size of the group, and the benzyl and allyl radicals are less firmly bound than methyl, but the problem is much more complex when the various groups are attached to atoms which differ from one another.

Alkaloids.

Pyridine Group.—Hitherto very little has been known concerning the alkaloids from *Lobelia inflata*, although H. Wieland, C. Schöpf, and W. Hermsen, a few years ago,[70] suggested formulæ for lobelanine, lobelanidine, and lobeline. As a result of more recent work,[71] however, much of the confusion which formerly existed has been removed and the inter-relationships of these products have been made clear : the earlier formulæ have been abandoned, and the accompanying structures, which represent comparatively simple pyridine derivatives, are now assigned to lobelanine (I; R = Me), lobeline (II), lobelanidine (III; R = Me), norlobelanine (I; R = H; formerly called " *iso*lobelanine "), and norlobelanidine (III; R = H). The alkaloid previously isolated and called " lobelidine," [72] is now shown to be *dl*-lobeline. The

$$CH_2$$
$$CH_2 \quad CH_2$$
$$COPh \cdot CH_2 \cdot CH \quad CH \cdot CH_2 \cdot COPh$$
$$(I.) \quad NR$$

$$CH_2$$
$$CH_2 \quad CH_2$$
$$COPh \cdot CH_2 \cdot CH \quad CH \cdot CH_2 \cdot CHPh \cdot OH$$
$$NMe \quad (II.)$$

$$CH_2$$
$$CH_2 \quad CH_2$$
$$OH \cdot CHPh \cdot CH_2 \cdot CH \quad CH \cdot CH_2 \cdot CHPh \cdot OH$$
$$NR \quad (III.)$$
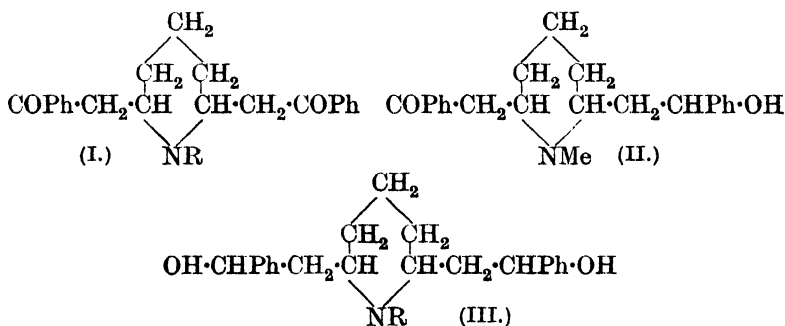
following are some of the outstanding facts in support of these formulæ : (*a*) Lobelanidine and lobeline can be oxidised to lobelanine, (*b*) further oxidation of lobelanine yields benzoic acid and 1-methylpiperidine-2 : 6-dicarboxylic acid, (*c*) lobelanine gives a dioxime which, after a Beckmann rearrangement, yields the dianilide of 1-methylpiperidine-2 : 6-diacetic acid, (*d*) the Hofmann degradation

[70] *Annalen*, 1925, **444**, 40; *A.*, 1925, i, 1087.
[71] H. Wieland and O. Dragendorff, *ibid.*, 1929, **473**, 83; *A.*, 1085; H. Wieland, W. Koschara, and E. Dane, *ibid.*, p. 118; *A.*, 1086.
[72] H. Wieland, *Ber.*, 1921, **54**, [*B*], 1784; *A.*, 1921, i, 802.

of lobelanine yields a neutral product, which, on subsequent reduction, gives 1 : 7-dibenzoyl-*n*-heptane or 1 : 9-dihydroxy-1 : 9-diphenyl-*n*-nonane according to the conditions, (*e*) reduction of norlobelanine with 1% sodium amalgam in dilute acetic acid gives norlobelanidine, which can be methylated to lobelanidine, and (*f*) acetophenone can be obtained from these alkaloids under a variety of conditions. The structures now assigned to these various alkaloids have been confirmed by synthetical means. For instance, 1 : 7-dibenzoyl-*n*-heptane-2 : 6-dione (IV), from the condensation
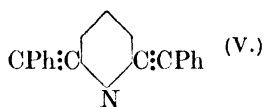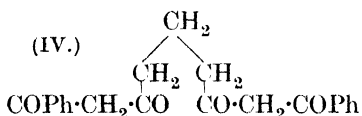
of ethyl glutarate and acetophenone, gave 2 : 6-di(benzoylmethylene)-piperidine on treatment with dry ammonia at 100°, and then various processes of reduction led to norlobelanidine and, after subsequent oxidation, to norlobelanine.[73] Again, 2 : 6-diphenyl-acetylenylpyridine (V), from the action of alcoholic potassium hydroxide on 2 : 6-distyrylpyridine tetrabromide, gave, with 50% (by vol.) sulphuric acid, 2 : 6-diphenacylpyridine, from which norlobelanidine was obtained by reduction.[74]

F. D. Chattaway and G. D. Parkes [75] have observed that nicotine tetrachloroiodide, $C_{10}H_{14}N_2,2HICl_4$, separates when a solution of the base in hydrochloric acid is added to a similar solution of iodine trichloride. This is a particularly well-crystallised derivative and affords an excellent method for isolating the alkaloid in a pure condition from tobacco, since the salt can be readily purified by recrystallisation from glacial acetic acid. The free base can then be obtained by decomposing this salt with sodium sulphite, and subsequently making the mixture alkaline. T. M. Lowry and W. V. Lloyd [76] have utilised the zinc chloride salt,

$$C_{10}H_{14}N_2,2HCl,ZnCl_2,H_2O,$$

for the purification of this alkaloid. It can be prepared from zinc chloride and the base in alcoholic hydrochloric acid, recrystallised from 60% alcohol, and finally decomposed with potassium hydroxide.

Quinoline Group.—Investigations into the nature of the products obtained from angostura bark have made considerable progress during the year. E. Späth and G. Papaioanou [77] have isolated a new phenolic alkaloid, galipoline, from this source. It was found

[73] H. Wieland and I. Drishaus, *Annalen,* 1929, **473**, 102; *A.*, 1086.
[74] G. Scheuing and L. Winterhalder, *ibid.*, p. 126; *A.*, 1086.
[75] *J.*, 1929, 1314.   [76] *Ibid.*, p. 1376.
[77] *Monatsh.*, 1929, **52**, 129; *A.*, 1087.

to contain one hydroxyl and two methoxyl groups, and, on methylation, yielded the related alkaloid, galipine, the structure of which was elucidated some time ago.[78] The relative positions of the hydroxyl and methoxyl groups were not at first apparent, but the fact that galipoline is 4-hydroxy-2-β-3′ : 4′-dimethoxyphenylethylquinoline (1) was finally established synthetically : 4-chloro-2-3′ : 4′-dimethoxystyrylquinoline, from the condensation of 4-chloro-2-methylquinoline and veratraldehyde, reacted with sodium benzyloxide to give the corresponding 4-benzyloxy-derivative, which, on reduction and subsequent hydrolysis, yielded galipoline.
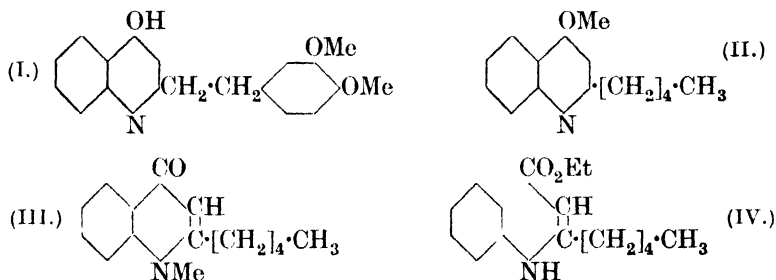
In addition, E. Späth and J. Pikl [79] have isolated a new base from the non-phenolic products of angostura bark, and have shown that it is 4-methoxy-2-n-amylquinoline (II). The main observations which indicated its structure were : (*a*) it was hydrolysed with difficulty to the corresponding phenolic base, which, after treatment with a mixture of phosphorus pentachloride and oxychloride, and reduction of the resulting chloro-compound, yielded 2-n-amylquinoline, the identity of which was established by synthesis; (*b*) by distillation of the methiodide of the new base in a vacuum 1-methyl-2-n-amyl-4-quinolone (III) was obtained, and this, on oxidation, yielded n-hexoic acid. The structure assigned to this new base was finally confirmed synthetically by condensing aniline with n-hexoylacetic ester at room temperature and heating the product (IV) for a short time at 250—255°. This process yielded the phenolic base corresponding to the alkaloid, which was itself then obtained by methylation with diazomethane.

iso*Quinoline Group*.—The isolation of an alkaloid, carnegine, $C_{13}H_{19}O_2N$, from *Carnegiea gigantea* has been described by G. Heyl,[80] who found that it contains two methoxyl groups. E. Späth [81]

[78] Compare *Ann. Reports*, 1924, **21**, 131.

[79] *Ber.*, 1929, **62**, [*B*], 2244.

[80] *Arch. Pharm.*, 1928, **266**, 668; *A.*, 201.

[81] *Ber.*, 1929, **62**, [*B*], 1021.

suggested that carnegine is 6 : 7-dimethoxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (III), and proved this view to be correct by
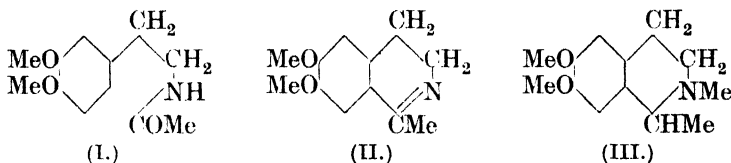
synthesising the alkaloid.   Aceto-β-3 : 4-dimethoxyphenylethyl-amide (1), when acted upon by phosphoric oxide in boiling toluene, gave 6 : 7-dimethoxy-1-methyl-3 : 4-dihydro*iso*quinoline [82] (II), the methiodide of which was reduced to carnegine.   The fact that the 6 : 7- and not the 7 : 8-dimethoxy-derivative resulted from this application of the Bischler–Napieralski reaction followed from the oxidation of (II) to *m*-hemipinic acid.   It has also been shown [83] that pectenine, an alkaloid isolated from *Cereus pecten aboriginum* by G. Heyl,[84] is in reality identical with carnegine.

Prompted by the fact that emetine appears to contain two 6 : 7-dimethoxytetrahydro*iso*quinoline residues joined through the 1-positions by a carbon chain,[85] R. Child and F. L. Pyman [86] have investigated the possibility of applying the Bischler–Napieralski reaction to the β-phenylethylamides and β-veratrylethylamides of the dibasic acids for the preparation of bisdihydro*iso*quinolines. Although the formation of even one of the two *iso*quinoline rings could not be brought about by applying the usual methods to the unsubstituted β-phenylethylamides (IV; R = H; $n = 1$ to 8), nevertheless the β-veratrylethylamides (IV; R = MeO; $n = 4$ to
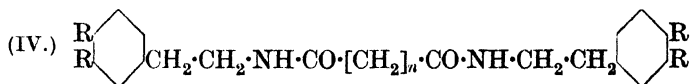
10) underwent intramolecular dehydration with the formation of the desired bisdihydro*iso*quinolines.   An examination of some of these products and the corresponding bistetrahydro*iso*quinolines formed by reduction indicated, however, that they did not possess the physiological properties of emetine.

It has been found that the condensation products of benzoyl-hydrazine and aromatic aldehydes undergo an intramolecular

[82]   E. Späth and N. Polgar, *Monatsh.*, 1929, **51**, 190.

[83]   E. Späth and F. Kuffner, *Ber.*, 1929, **62**, [*B*], 2242.

[84]   *Arch. Pharm.*, 1901, **239**, 459.

[85]   Compare *Ann. Reports*, 1927, **24**, 174.

[86]   *J.*, 1929, 2010.
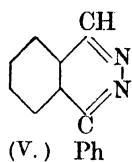
dehydration, which is reminiscent of the Bischler-Napieralski reaction, on treatment preferably with amyl-alcoholic hydrogen chloride, and yield phthalazines [87] (V). These phthalazines, on hydrolysis, yield hydrazine and o-aldehydo-ketones, and the process affords a valuable synthetical method for preparing substances of the latter type.

E. Späth and N. Polgar [88] have observed that the 3 : 4-dihydro-*iso*quinolines obtained by the dehydration of substituted acyl-β-phenylethylamides can be dehydrogenated with palladium-black at 150—180° to the corresponding *iso*quinoline bases, several of which they have prepared in this way.

Hitherto little has been known regarding the constitution of oxyacanthine, one of the alkaloids isolated from *Berberis* spp., and even its molecular formula has been in doubt.[89] More recent work, however, has enabled E. Späth and J. Pikl [90] to advance the formula (VI) for this alkaloid, although much yet remains to be done before its constitution is definitely settled. Three oxygen atoms are accounted for as methoxyl groups, one as a phenolic hydroxyl group, and the remaining two as ether linkages. An application of the Emde degradation process gave results which suggested the presence of two *iso*quinoline nuclei. The attachment of the diphenyl ether residue to each *iso*quinoline nucleus through methylene groups was indicated by the isolation of 3-phenoxy-4-methoxy-
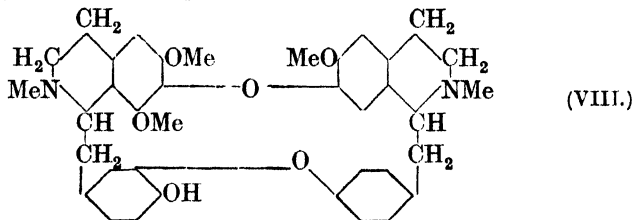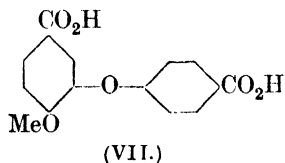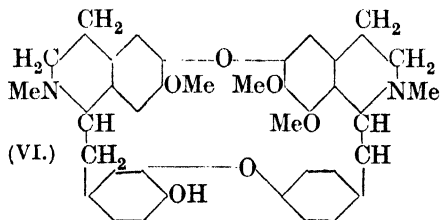
[87] J. S. Aggarwal, N. L. Darbari, and J. N. Rây, *J.*, 1929, 1941.

[88] *Monatsh.*, 1929, **51**, 190; *A.*, 578.

[89] E. Späth and A. Kolbe, *Ber.*, 1925, **58**, [*B*], 2280; *A.*, 1926, 82; J. Gadamer and W. von Bruchhausen, *Arch. Pharm.*, 1926, **264**, 193; *A.*, 1926, 627.

[90] *Ber.*, 1929, **62**, [*B*], 2251.

benzene-1 : 4'-dicarboxylic acid (VII) by the oxidation of the
product obtained from oxyacanthine methyl ether by the Hofmann
degradation process.   A similar procedure applied to oxyacanthine
ethyl ether yielded 3-phenoxy-4-ethoxybenzene-1 : 4'-dicarboxylic
acid, which fixed the position of the phenolic hydroxyl group.   The
publication of this work on oxyacanthine by Späth and Pikl brought
forth a paper by F. von Bruchhausen and H. Schultze,[91] who had
arrived independently at a very similar formula (VIII) for this
alkaloid, as a result of closely related oxidation experiments, so
that agreement seems to have been reached upon the main features.
There are, in consequence, several points of resemblance between
oxyacanthine and the alkaloids curine and *iso*chondodendrine.[92]
Von Bruchhausen and Schultze also mention a new non-phenolic
alkaloid, $C_{19}H_{22}ON_2$, which they have isolated in small quantities
from *Berberis vulgaris*.

Aporphine Group.—A series of reactions, which involves the
Bischler–Napieralski synthesis and has previously been utilised
for the preparation of a number of aporphine derivatives,[93] has
now been applied by R. K. Callow, J. M. Gulland, and R. D.
Haworth[94] to the preparation of 2 : 3 : 6 : 7- and 3 : 4 : 6 : 7-tetra-
methoxyaporphine (IV and V).   For instance, 6'-nitro-3' : 4'-di-
methoxyphenylaceto-β-2 : 3-dimethoxyphenylethylamide   (I)   has
been converted by the action of phosphorus pentachloride in cold
chloroform   into   6'-nitro-3' : 4' : 5 : 6-tetramethoxy-1-benzyl-3 : 4-
dihydro*iso*quinoline (II), the methiodide of which, on reduction
with zinc dust and hydrochloric acid, gave the amine (III).
dl-2 : 3 : 6 : 7-Tetramethoxyaporphine (IV) was subsequently ob-
tained by diazotisation in methyl-alcoholic sulphuric acid.   A
parallel series of reactions led to *dl*-3 : 4 : 6 : 7-tetramethoxyapor-
phine (V).   The synthesis of the former of these two aporphines is

(I.)   (II.)   (III.)
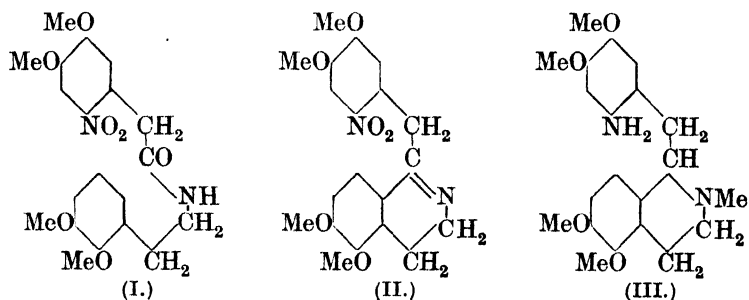
[91] *Arch. Pharm.*, 1929, **267**, 617.
[92] See *Ann. Reports*, 1928, **25**, 190.
[93] Compare *Ann. Reports*, 1928, **25**, 186.   [94] *J.*, 1929, 658.

interesting in view of its bearing on the constitution of lauro-tetanine. K. Gorter assigned the structure (IV) to "*iso*glaucine,"

MeO

MeO
CH_2
CH
NMe
MeO
CH_2
MeO CH_2
(IV.)

MeO
MeO
CH_2
CH
NMe
MeO
CH_2
MeO CH_2
(V.)

McO
RO
CH_2
CH
MeO
NMe
CH_2
CH_2
(VI.)
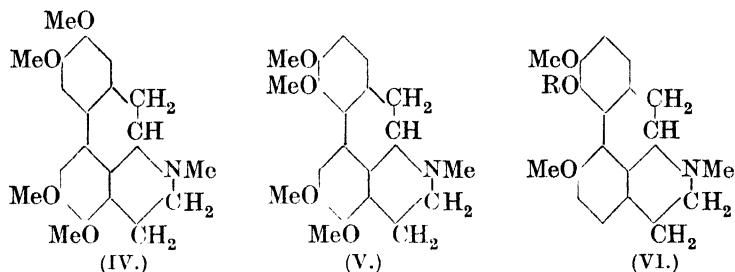
the methylation product of laurotetanine, but it has recently been shown [95] that "*iso*glaucine" was impure glaucine, and confirmation of this is now derived from the fact that the reactions of the syn-thetical product (IV) do not resemble those of "*iso*glaucine."

The formula (VI; R = H) has been allotted to *iso*thebaine,[96] isolated from *Papaver orientale*, and, with a view to testing this, attempts have been made [97] to apply analogous synthetical methods to the preparation of *iso*thebaine methyl ether (VI; R = Me). It was not possible, however, in the case of 2'-nitro-3' : 4'-dimethoxy-phenylaceto-β-4-methoxyphenylethylamide (VII; R = MeO), to convert the amide into an *iso*quinoline derivative, probably on account of the absence from the 3-position of a strongly *p*-directing group. General experience has certainly indicated that it may be very difficult to carry out a Bischler–Napieralski reaction, except with compounds containing an activating group, and the same explanation may be given of the failure to obtain a dihydro*iso*-quinoline derivative from 2'-nitro-3' : 4'-dimethoxyphenylaceto-β-phenylethylamide (VII; R = H) by the action of phosphorus pentachloride in an attempt to synthesise *apo*morphine dimethyl

MeO
MeO
NO_2 CH_2
CO
R
NH
CH_2
CH_2
(VII.)

MeO
MeO
CH_2
CH
NMe
CH_2
CH_2
(VIII.)

MeO
MeO
NO_2 CH_2
C
N
CH_2
CH_2
(IX.)
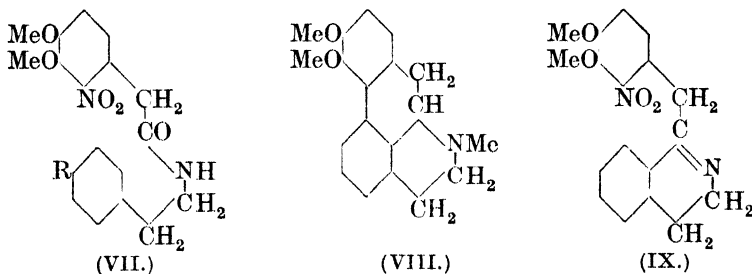
[95] See *Ann. Reports*, 1928, **25**, 188.
[96] W. Klee, *Arch. Pharm.*, 1914, **252**, 211; *A.*, 1914, i, 1086.
[97] R. K. Callow, J. M. Gulland, and R. D. Haworth, *J.*, 1929, 1444.

ether [98] (VIII). The position in regard to the latter instance is, however, somewhat uncertain, since E. Späth and O. Hromatka [99] appear to have succeeded in obtaining the dihydro*iso*quinoline (IX) from this amide by the use of phosphoric oxide in boiling xylene, and to have proceeded subsequently to the synthesis of *apo*morphine dimethyl ether.

Although the condensation of an *o*-nitrotoluene derivative with the appropriate 1-hydroxy-2-methyl-1 : 2-dihydro*iso*quinoline has provided the first step in the synthesis of several aporphine bases, J. M. Gulland and C. J. Virden [1] have found that this reaction fails when applied to 2-nitrohomoveratrole (X), but, by utilising 2-nitro-3 : 4-dimethoxyphenylacetonitrile, in which the hydrogen atoms of the methylene group have received additional activation, it has been possible to prepare the bases (XI), (XII; $R = R' =$ MeO), and (XII; $R = $ MeO; $R' = $ H). Further progress towards

(X.)   (XI.)   (XII.)
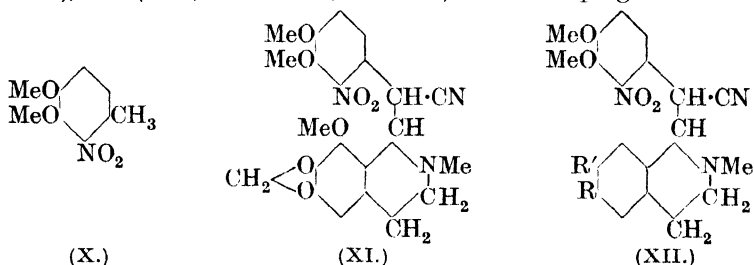
the corresponding 3 : 4-dimethoxyaporphine derivatives, which involves reduction of the nitro-group, was found to be impossible, however, on account of the readiness with which these bases were hydrolysed into the original reagents by dilute acids or alkalis. In opposition to the experience of these authors is the synthesis of *apo*morphine dimethyl ether described by H. Avenarius and R. Pschorr,[2] who claim to have condensed together 2-nitro-3 : 4-dimethoxyphenylacetonitrile (XIII) and 1-hydroxy-2-methyl-1:2:3:4-tetrahydro*iso*quinoline (XIV) with the formation of the nitrile (XII; $R = R' = $ H), which, after hydrolysis, removal of carbon

(XIII.)   (XIV.)   (XV.)
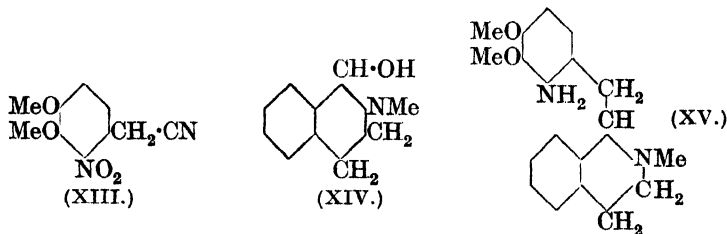
[98] J. M. Gulland, R. D. Haworth, C. J. Virden, and R. K. Callow, *J.*, 1929, 1666.

[99] *Ber.*, 1929, **62**, [B], 325.   [1] *J.*, 1929, 1791.   [2] *Ber.*, 1929, **62**, [B], 321.

dioxide and subsequent reduction, gave the base (XV). Diazotisation, followed by the addition of copper powder, is said to yield *apo*morphine dimethyl ether (VIII). These reactions, however, may need further investigation, since Gulland and Virden failed in several attempts to prepare *apo*morphine dimethyl ether by this method, and, as these authors point out, Avenarius and Pschorr claim to have established the identity of their synthetical *dl-apo*morphine dimethyl ether methiodide with the lævorotatory methiodide from natural sources.

Diisoquinoline Group.—The condensation of methoxy- or methylenedioxy-bases of the type (I; X or Y = OMe, or XX or YY = O_2CH_2) with formaldehyde has always given derivatives of the type (II), by ring closure in the 2-position, and these reactions have not provided a route for the synthesis of alkaloids of the tetrahydroberberine class (III), which would require ring closure in the 6-position. E. Späth and E. Kruta [3] have now found, however,

(I.)   (II.)   (III.)
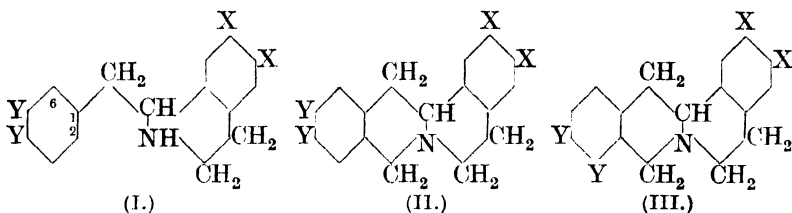
that tetrahydropapaveroline (I; X = Y = OH), in which there are four free hydroxyl groups, condenses with formaldehyde to give a product which, on methylation with diazomethane, yields equal amounts of both the corresponding bases, norcoralydine (II; X = Y = OMe) and tetrahydropalmatine (III; X = Y = OMe). The view is expressed, therefore, that in the plant the alkaloids of this class are produced from hydroxy-derivatives of the type (I) by condensation with formaldehyde, followed by alkylation and subsequent oxidation to the quaternary base. By taking advantage of these observations, the same authors [4] have developed a synthesis of *meso-* and *r*-corydaline, the two stereoisomerides of the formula (IV). Papaverine was condensed with formaldehyde to yield

(IV.)   (V.)
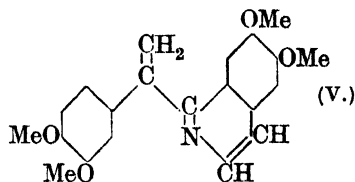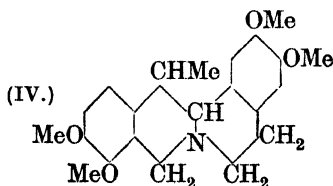
[3] *Monatsh.*, 1928, **50**, 341; *A.*, 201.   [4] *Ber.*, 1929, **62**, [*B*], 1024.

methylenepapaverine (V), which was reduced catalytically to methylpapaverine (VI). This, on electrolytic reduction, gave a mixture of the two racemic methyltetrahydropapaverines (VII), which was demethylated, condensed with formaldehyde, and subse-

quently re-methylated with diazomethane to give a basic mixture, from which *meso*corydaline was isolated by crystallisation from ether at 0°. The bases of the tetrahydropalmatine type present in the mother-liquor were then separated from the other basic products by dehydrogenating them with hot alcoholic iodine, removing the quaternary salts, thus formed, in aqueous solution, and reducing them back to the tetrahydro-bases with zinc and acetic acid. By dissolution of these bases in dilute hydrochloric acid and fractional precipitation with potassium bromide, a hydrobromide was obtained which yielded a small quantity of *r*-corydaline.
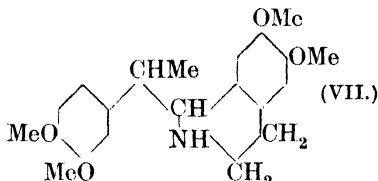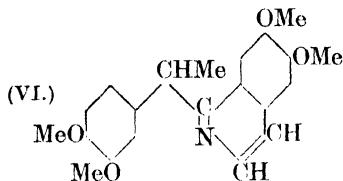
The structure of coptisine (VIII), an alkaloid from *Coptis japonica*, and its relationship to palmatine (IX), of which it is the di-methylene-dioxy-analogue, were made clear as a result of the work of Z. Kitasato,[5] who transformed it into the latter alkaloid. E. Späth and
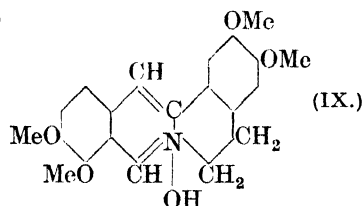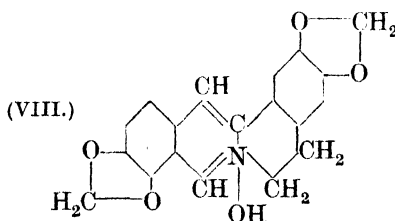
R. Posega[6] have now explored the possibilities of synthesising coptisine from substances related to it. Attempts to prepare tetrahydrocoptisine (III; $XX = YY = O_2CH_2$) from palmatine chloride by demethylation, followed by methylenation and subsequent reduction, failed, but, by demethylating tetrahydropalmatine and methylenating the product under the appropriate conditions, the authors obtained a small amount of tetrahydrocoptisine. Another route was to proceed from protopine (X) by reduction with sodium amalgam to the corresponding secondary alcohol,

[5] *Proc. Imp. Acad. Tokyo*, 1926, **2**, 124; *A.*, 1926, 1160,

[6] *Ber.*, 1929, **62**, [B], 1029; *A.*, 707.

which was converted into the salt (XI) by evaporating its solution in hydrochloric acid and then, on subsequent distillation of the corresponding iodide in a vacuum, into tetrahydrocoptisine. The latter base can readily be converted into coptisine iodide by heating
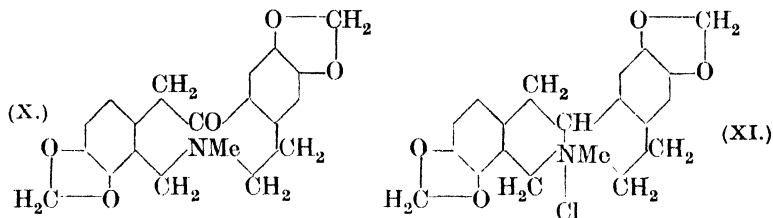
it with iodine in alcoholic solution. R. D. Haworth and W. H. Perkin,[7] before the isolation of coptisine had been described, prepared its tetrahydro-derivative (III; $XX = YY = O_2CH_2$) during their synthesis of protopine.

Continuing the investigation of the preparation and properties of the simpler substances of the palmatine-berberine type,[8] S. N. Chakravarti and W. H. Perkin [9] have applied the reactions used in the synthesis of oxyberberine [10] to the production of 3 : 10-dimethoxytetrahydroprotoberberine (XV). 4-Methoxyphthalidecarboxy-β-m-methoxyphenylethylamide (XIII), obtained by acting upon the acid chloride of 4-methoxyphthalidecarboxylic acid (XII) with β-m-methoxyphenylethylamine, was converted by heating with
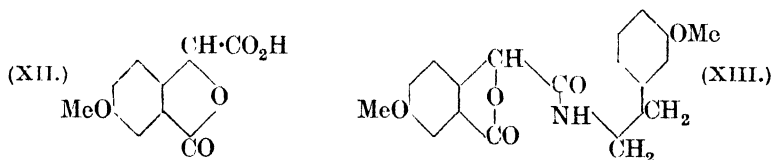
phosphorus oxychloride into a basic substance, which yielded 3 : 10-dimethoxyoxyprotoberberine (XIV) on reduction with zinc
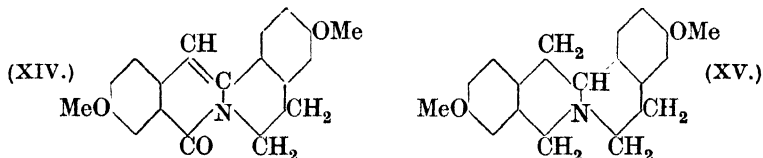
[7] J., 1926, 1769; Ann. Reports, 1926, 23, 167.

[8] S. N. Chakravarti, R. D. Haworth, and W. H. Perkin, J., 1927, 2265, 2275; Ann. Reports, 1927, 24, 171.

[9] J., 1929, 196.

[10] W. H. Perkin, J. N. Rây, and R. Robinson, J., 1925, 127, 740; Ann. Reports, 1925, 22, 146.

dust and acetic acid. Further reduction by electrolytic means gave
3 : 10-dimethoxytetrahydroprotoberberine (XV), which has the
characteristic features of its 3 : 11-isomeride.

Morphine Group.—A short time ago the formula (I) was assigned
by K. Goto [11] to the alkaloid sinomenine, isolated from *Sinomenium
acutum*, but this has now been abandoned in favour of (II) or (III).[12]
Sinomenol, obtained from the alkaloid by potash fusion, was
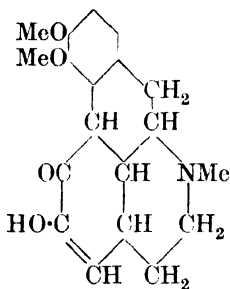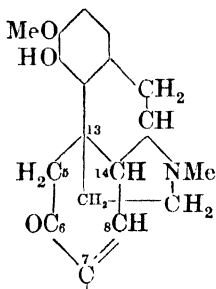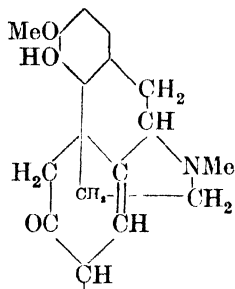
(I.)   OMe (II.)   OMe (III.)

originally thought to be 3 : 4-dihydroxy-5 : 6-dimethoxyphenanthr-
ene, but it has now been shown synthetically by Pschorr's method
that its dimethyl ether is 3 : 4 : 6 : 7-tetramethoxyphenanthrene.
Furthermore it is concluded from the reactions of sinomenine that
it must be closely related to thebainone, and sinomenol is now
regarded as 4 : 6-dihydroxy-3 : 7-dimethoxyphenanthrene (IV). The
point of attachment of the methylaminoethyl chain in sinomenine
seems to be uncertain, both C5 and C13 being admitted as possi-
bilities, and agreement does not seem to have been reached con-
cerning the exact location of the double linkage, which may be in
the 7 : 8- or 8 : 14-positions. The action of mild oxidising agents on
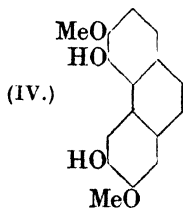
(IV.)
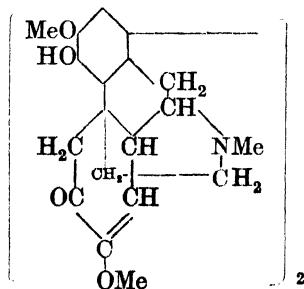
(V.)

[11] *Proc. Imp. Acad. Tokyo,* 1926, **2,** 7, 167; *A.,* 1926, 1160; compare *Ann.
Reports,* 1926, **23,** 171.
[12] H. Kondo and E. Ochiai, *J. Pharm. Soc. Japan,* No. 538, 1015; No. 539,
20; K. Goto, *Bull. Chem. Soc. Japan,* 1929, **4,** 103; K. Goto and H. Sudzuki,
ibid., pp. 107, 163, 244; *A.,* 830, 944; H. Kondo and E. Ochiai, *Annalen,*
1929, **470,** 224; *A.,* 1088.

sinomenine gives a mixture of disinomenine and ψ-disinomenine, to which formulæ of the type (V) are assigned and which may differ in the point of attachment of the methylaminoethyl chain. The former is said to accompany sinomenine in nature. K. Goto and H. Sudzuki [13] have described the isolation of two new alkaloids, acutumine and sinactine, from *Sinomenium acutum*, although the quantities obtained have as yet been insufficient for any definite views to be advanced concerning their structure. The alkaloids so far described from this source number five : sinomenine, diversine, disinomenine, acutumine, and sinactine.

H. Wieland and L. F. Small [14] have pointed out that α-thebaizone, obtained by the action of ozone on thebaine, must have the constitution (VI), if the Gulland and Robinson formula (VII) for
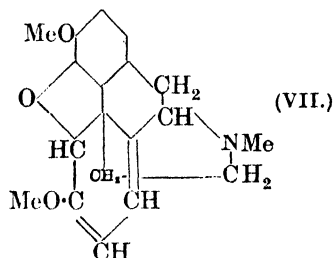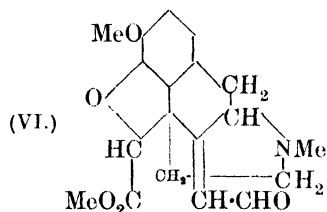
thebaine is accepted. The results obtained in an extensive investigation of the reactions of α-thebaizone and related substances have been found to be in agreement with these structural views, and confirm the thebaine formula.

Strychnine.—In a further communication dealing with the complex chemistry of the derivatives of strychnine, W. H. Perkin and R. Robinson [15] have pointed out that the new formula recently
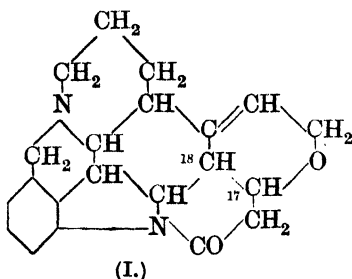
advanced for this alkaloid [16] needs slight modification. In its revised form (I) the heterocyclic system containing the ether oxygen is attached to C17, and not to C18. B. K. Blount, W. H. Perkin, and S. G. P. Plant,[17] from a study of a large number of partly reduced polycyclic compounds, have observed that 1-acyl-1 : 2 : 3 : 4-tetrahydroquinoline derivatives and 1-acyl-2 : 3-dihydroindole derivatives

[13] *Bull. Chem. Soc. Japan*, 1929, **4**, 220.

[14] *Annalen*, 1928, **467**, 17; *A.*, 81.　　　[15] *J.*, 1929, **964**.

[16] R. C. Fawcett, W. H. Perkin, and R. Robinson, *J.*, 1928, **3089**; compare *Ann. Reports*, 1928, **25**, 193.　　　[17] *J.*, 1929, **1975**.

are characterised and distinguished from one another by colour reactions with potassium dichromate in 65% sulphuric acid. Members of the former class give an intense crimson colour which persists for some time, and those of the latter type give an intense, but rather transient, blue or violet-blue colour. The corresponding de-acylated bases give no such intense colour under these conditions. Strychnine gives the colour reaction of the 1-acyl-2 : 3-dihydroindoles, and it is interesting to note that this skeleton is present in the new formula for this alkaloid, but it was absent from the original formula of Perkin and Robinson.

A new alkaloid, vomicine, obtained as a by-product in the isolation of strychnine, has been described by H. Wieland and G. Oertel.[18] It has the molecular formula $C_{22}H_{24}O_4N_2$ and appears to contain an oxide ring, as in strychnine.

Lupin Alkaloids.—The chemistry of these substances has been the subject of further interesting developments, the chief of which has been the assignment of a structural formula to lupinine. From an examination of the products derived from lupinine by exhaustive methylation and subsequent reduction, P. Karrer, F. Canal, K. Zohner, and R. Widmer[19] consider that this alkaloid may be represented by the formula (I). The action of phosphorus pentabromide on the fully reduced, nitrogen-free product has given what is apparently δ-bromomethylnonane, since the unsaturated hydrocarbon obtained by adding trimethylamine and subsequently distilling the corresponding hydroxide, yielded, on treatment with
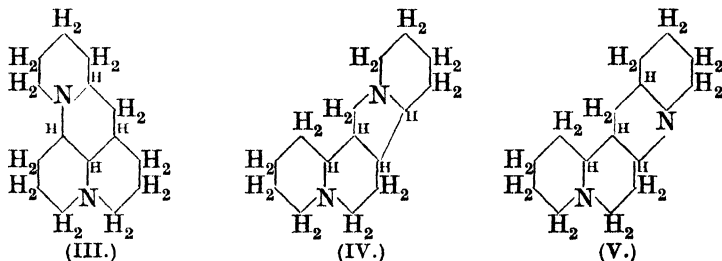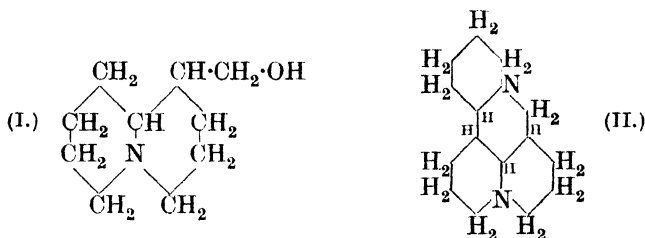
[18] *Annalen*, 1929, **469**, 193; *A.*, 708.
[19] *Helv. Chim. Acta*, 1928, **11**, 1062; *A.*, 200.

ozone, *n*-propyl *n*-amyl ketone. Although this formula is by no means established, the known reactions of lupinine can be explained with its aid. These authors have expressed the view that sparteine may possibly be represented as a condensation product of lupinine and piperidine, for which the alternative structures (II, III, IV, and V) can be evolved.

G. R. Clemo and R. Raper [20] have found, however, that a structural change in the lupinine molecule is possible during the Hofmann degradation process, and, furthermore, they show that it is difficult to reconcile some of the known facts in the chemistry of sparteine and the closely related lupanine with any of these alternative formulæ advanced by Karrer and his co-workers for sparteine. K. Winterfeld [21] also re-affirms the belief that sparteine must be represented as a quinuclidine derivative, in which case these formulæ cannot serve for this alkaloid.

Tropane Group.—The observation that the hydrolysis of bella-

$$
\begin{array}{ccc}
CH_2 & \!\!-\!CH\!-\!\! & CH_2 \\
| & NMe & CHCl \\
CH_2 & \!\!-\!CH\!-\!\! & CH_2
\end{array}
$$
(1.)

donnine with concentrated hydrochloric acid at 140° leads to " bellatropine," $C_8H_{15}ON$, a new isomeride of tropine,[22] has now been shown to be incorrect.[23] The product of the reaction is apparently 3-chlorotropane (I), the analogous 3-bromotropane being obtained if hydrobromic acid is used in the hydrolysis.

3-*Membered Rings.*

During the past twenty years there has been a gradually increasing tendency to disbelieve in the existence of 3-membered rings unless they contain at least two carbon atoms. This movement originated in the work of Angeli, as a result of which open-chain configurations for the azoxy-compounds and the *N*-ethers of the oximes replaced the older ring structures. Receiving considerable impetus from the investigations of Thiele and Staudinger, similar views, involving the formulæ (I and II), have in recent years become

$$\text{(I.)}\quad R_2C{=}N{\rightarrow}N \qquad\qquad R{\cdot}N{=}N{\rightarrow}N \quad \text{(II.)}$$
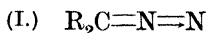
widely accepted for the aliphatic diazo-compounds and the azides. These two classes have some points in common and it is probable that, in any case, they have analogous formulæ. In spite of very extensive investigations into the chemistry of the aliphatic diazo-compounds there is no really conclusive evidence for the open-chain formula, and an examination of the physical properties of

[20] *J.*, 1929, 1927.   [21] *Arch. Pharm.*, 1929, **267**, 433; *A.*, 1186.

[22] O. Hesse, *Annalen*, 1893, **277**, 295.

[23] M. Polonovski and M. Polonovski, *Compt. rend.*, 1928, **188**, 179; *A.*, 335; *Bull. Soc. chim.*, 1929, [iv], **45**, 304; *A.*, 830.

these substances has now indicated that a return to the original ring structures (III and IV) may have to be made. H. Lindemann and H. Thiele [24] determined the parachors of certain azides and

$$(\text{III.}) \quad R_2C{<}{\overset{N}{\underset{N}{\vert\vert}}} \qquad\qquad RN{<}{\overset{N}{\underset{N}{\vert\vert}}} \quad (\text{IV.})$$
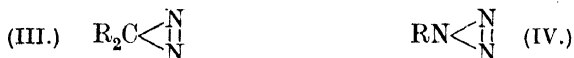
found support for the ring structure. N. V. Sidgwick [25] has pointed out, however, that these results are not really conclusive, although for other reasons he supports the older formulations. Thus, since the presence of a co-ordinate link causes a rise in the boiling point, if the aliphatic diazo-compounds and the azides have the cyclic configurations, they should boil at approximately the same temperatures as the corresponding halides, but an open-chain structure would demand boiling points close to those of the nitro-compounds. With these considerations in mind, an examination of the boiling points of a large number of aliphatic diazo-compounds and azides has pointed quite definitely to the older formulæ.

S. G. P. PLANT.

[24] Ber., 1928, **61**, [B], **1529**; A., 1928, 937.   [25] J., 1929, 1108.

ANALYTICAL CHEMISTRY.

The output of investigations in analytical chemistry increases in volume, but there is no outstanding discovery to be reported. Progress continues to be made in the utilisation of specific reactions for various kations and anions, and micro-chemical methods of detection and estimation are being extended and developed, as is shown by the publication of a volume of " Mikrochemie " dedicated to Pregl (1929). The object of much of the qualitative investigations is the formulation of such specific tests or reactions for each element or group. As examples of these tests we have Feigl's for silver by means of p-dimethylaminobenzylidenerhodanine, which depends on the formation of a red precipitate even in dilutions where the silver chloride precipitation cannot be observed; this reagent also reacts with mercury, but becomes specific for silver when potassium cyanide is present.[1] Again, the detection of aluminium by means of the violet colour given by " eriochromcyanin R. conc." or the green fluorescence with morin in methyl-alcoholic solution is extraordinarily delicate, and is not interfered with by a large excess of cobalt, nickel, or similar metals. The delicacy of these tests is such that it becomes difficult to be certain that the water and reagents themselves do not give positive reactions for aluminium. In this connexion there are now available specific reactions or colour tests for silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, iron, aluminium, chromium, manganese, nickel, cobalt, zinc, barium, strontium, calcium, magnesium, potassium, sodium, fluoride, chloride, bromide, iodide, sulphide, thiosulphate, sulphite, sulphate, nitrite, nitrate, phosphate, borate, carbonate, cyanide, ferrocyanide, ferricyanide, thiocyanate, and oxalate. This comprehensive list of kations and anions has been set out in a systematic way for rapid examination by a spot test method.[2]

Increasing use is likewise being made of the formation of complex compounds for both the detection and the estimation of metals and certain groups, frequently by micro-chemical examination. Cupferron (nitrosophenylhydroxylamine) thus finds extended use for barium and uranyl kations because of the characteristic crystals

[1] K. Heller and P. Krumholz, *Mikrochem.*, 1929, **7**, 213; *A.*, 900.
[2] G. Gutzeit, *Helv. Chim. Acta*, 1929, **12**, 713, 829; *A.*, 898, 1254.

formed.[3] Characteristic crystalline compounds are also formed by
means of ammonium thiocyanate and aniline from ammoniacal
solutions of copper, cadmium, and nickel, of the general type
$2(C_6H_5 \cdot NH \cdot HSCN), M(NH_3)_4(SCN)_2$.[4] These compounds recall the
pyridine-thiocyanates of Spacu and his co-workers, which have
found application in the detection and estimation of a number of
metals. It is specially important to note that copper pyridine
thiocyanate, $[Cu(C_5H_5N)_2](SCN)_2$, dissolves in chloroform, giving a
green solution, so that this metal may by this means be determined
in the presence of all those metals which give white compounds.[5]
Neutral solutions of mercury and cadmium when treated with
potassium iodide give precipitates with solutions of ethylenediamine
copper nitrate, $(Cu \ en_2)(NO_3)_2, 2H_2O$, of the type $(XI_4)(Cu \ en_2)$, and
these are used to determine mercury or cadmium by macro- or
micro-methods.[6] Other organic bases are available for the form-
ation of these complex metallic compounds, e.g., aminopyrine,
8-hydroxyquinoline, cinchonine, and quinoline, and their use may be
expected to extend.

The determination of mercury as $(HgI_4)(Cu \ en_2)$ is rapid,[7] but the
method of precipitation as $HgCr_2O_7, 2C_5H_5N$ has the advantage of
employing only common laboratory reagents, and it is rapid and
accurate as well, yielding a precipitate readily collected and
handled.[8] This method is suitable for comparatively large quan-
tities of mercury, but a more frequent problem is the accurate deter-
mination of small amounts in organic and inorganic materials. It
has been found that hypophosphorous acid will reduce mercury salts
in the cold and the metal may be readily determined with $0.01N$-
iodine solution, provided that a slight excess of $0.01N$-thiosulphate
solution is used and the excess determined. The value of the
method is increased by the fact that it is applicable to solutions
containing copper and iron salts and to the liquid obtained by
oxidation of organic matter as in the ordinary Carius method for
halogens.[9] The estimation of minute quantities of mercury may be
as accurately made by the use of diphenylcarbazone, which gives the
characteristic blue liquid, as by the formation of mercuric iodide;
but the difficulty in the first place is to collect the trace of mercury
from a liquid which contains substances capable of vitiating the
determination. This may conveniently be accomplished by
electrolysis with small gold cathodes, which can then be introduced

[3] A. Martini, *Mikrochem.*, 1928, **6,** 152; *A.,* 164.
[4] *Idem, ibid.,* 1929, **7,** 30.
[5] G. Spacu and J. Dick, *Z. anal. Chem.,* 1929, **78,** 241; *A.,* 1259.
[6] G. Spacu and G. Suciu, *ibid.,* **77,** 334, 340; **78,** 244; *A.,* 901, 1259.
[7] *Idem, ibid.*   [8] G. Spacu and J. Dick, *ibid.,* 1929, **76,** 273; *A.,* 416.
[9] R. Robinson, *Analyst,* 1929, **54,** 145; *A.,* 531.

into glass tubes and heated with chlorine, furnishing mercuric chloride; or the mercury may be volatilised by heating and detected as iodide. Perhaps the most delicate test for the volatilised mercury is Nordlander's selenium sulphide method, for the diphenylcarbazone method in our experience requires very careful adjustment of the acidity of the test solutions (see also p. 193).

In mineral analysis the determination of silica is always liable to give low results because of the difficulty of deciding when the last portions of silica have been rendered insoluble in the reagents used. It is therefore of some value to have the molybdenum-stannite reaction which is capable of detecting traces of silica. The neutral solution is treated with an excess of neutral ammonium molybdate, the mixture rendered faintly alkaline, and sodium stannite added. This has the effect of reducing polysilico-molybdic acid to a blue lower oxide of molybdenum, and the test can be used in the presence of not too great an amount of phosphate.[10]

For some time past a great deal of attention has been devoted to the separation of calcium and magnesium. When the metal ions are present in substantial quantities the oxalate method of separation seems to be the best, both for convenience and accuracy. This cannot, however, be secured unless certain conditions are strictly adhered to. It is certain that if too much ammonium oxalate is used some magnesium will be precipitated with the calcium, and it will also be impossible to precipitate all the magnesium in the filtrate unless the troublesome procedure of expelling the ammoniacal salts is adopted. As a rule, two precipitations of the calcium are desirable to effect the separation, but it is stated that one will suffice if the solution of the two metals is precipitated at 70° with only a small excess of ammonium oxalate.[11] A study of the supersaturation of solutions of magnesium oxalate, however, indicates that co-precipitation of magnesium oxalate with calcium oxalate is likely to result if the concentration of magnesium ions or the temperature is too high.[12] Nevertheless, it has again been shown that excess of ammonium oxalate is wanted when magnesium preponderates and has to be retained in solution while the calcium is being precipitated.[13] On the other hand, for the micro-separation of calcium, an acetic acid solution is preferable for precipitating the calcium as oxalate in the first place, the magnesium being recovered by precipitation with 8-hydroxyquinoline. Much controversy has resulted from the

[10] F. Oberhauser and J. Schormüller, *Z. anorg. Chem.*, 1929, **178**, 381; *A.*, 414.

[11] O. Røer, *Tidsskr. Kjemi Berg.*, 1929, **9**, 27; *A.*, 530.

[12] Z. Herrmann, *Z. anorg. Chem.*, 1929, **182**, 395; *A.*, 1159.

[13] W. T. Hall, *J. Amer. Chem. Soc.*, 1928, **50**, 2704; *A.*, 1928, 1347.

discussion of the best method of conversion of magnesium ammonium phosphate into magnesium pyrophosphate in the determination of magnesium. It has been shown that the refinements, such as evaporation with nitric acid to oxidise " carbon " in the precipitate and similar devices, are unnecessary,[14] and we agree with this conclusion.

It is not usual to consider a volumetric method of analysis as entitled to the description " beautiful," but this designation may fairly be applied to the adsorption indicators developed by Fajans and his co-workers. As a lecture experiment, the reversible colour changes of eosin, when colloidal silver bromide is present, on addition of silver or bromine ions are striking. The competition of the indicator anion and of the halogen ion for adsorption on the silver halide leads to nice discrimination in the choice of adsorption indicators, as, for example, fluorescein for titration of chlorides, and eosin for bromides and iodides. Thus Victoria-violet, chrome-green G, bromo-phenol-blue, and bromocresol-purple can be used to determine either the separate halogens or chloride and iodide when together.[15]

A subject of much interest in the practical use of indicators for the colorimetric determination of p_H values is the magnitude of the salt error and the effect of the dissociation of the indicator itself when attempts are made to determine the p_H of an unbuffered liquid. The error becomes greater as the dissociation constant of the indicator is decreased, so that those indicators become most serviceable which can be used in very low concentrations.[16] The complexity of this salt error and its dependence on the nature of the buffer solution may further be seen from a consideration of the corrections which have to be applied for indicators in citrate solutions. It is fortunate that both methyl-orange and methyl-red give quite small salt errors in various conditions of the solutions. This circumstance permits of their use in colorimetric p_H determinations within their range.[17] The salt error arises in practice in various ways ; for example, when equal colours are given with an indicator by a solution of sodium hydroxide and some buffer, say a borate, it does not necessarily follow that the p_H is the same when determined electrometrically. Neutralisation of the indicator itself cannot be responsible for this effect except to a small extent, for errors as high as 2 units of p_H may be obtained with phenol-red and borate mixtures. This is attributed to the salt error arising from the indicators themselves

[14] (Miss) A. W. Epperson, *J. Amer. Chem. Soc.*, 1928, **50**, 321; *A.*, 1928, 386.

[15] H. A. J. Pieters, *Chem. Weekblad*, 1929, **26**, 6; *A.*, 161.

[16] J. Eisenbrand, *Pharm.-Ztg.*, 1929, **74**, 989, 1287; *A.*, 1157, 1255.

[17] I. M. Kolthoff, *J. Physical Chem.*, 1928, **32**, 1820; *A.*, 161.

and is inappreciable in certain cases, *e.g.*, with thymol-violet and alizarin-yellow G.[18]

Of special interest and practical importance in acidimetric determinations is the fact that certain substances show a definite alteration in their ultra-violet fluorescence under the influence of a variation of the hydrogen-ion concentration. Quinine, for example, shows two sharp colour changes at p_H 6 and 9·5, and is therefore available for use in the titration of bases, both strong and weak; α- and β-naphthols have been similarly used.[19] As it is easy to construct a suitable cabinet fitted with so-called ultra-violet glass for use with a mercury arc lamp, the method becomes one of some delicacy and ease of manipulation.

Inorganic Analysis.

Qualitative.—Specific and special reactions, mainly colour reactions with organic reagents, are described for the commoner anions and kations.[20] Some new metallic complexes of cupferron,[21] of thiocyanic acid,[22] and of hexamethylenetetramine [23] have been examined. Micro-reactions may often be carried out with advantage using a gel as medium.[24] The tests for ferrous and ferric iron with ferri- and ferro-cyanide respectively are influenced by the presence of fluorides owing to the depression of hydrogen-ion concentration,[25] and this has been utilised to prevent the interference of ferric iron with the ferrocyanide test for copper;[26] similarly the delicacy of the thiocyanate test for iron is affected by the presence of other salts.[27] Conversely, the thiocyanate test may be applied for the detection of sulphur, free or in the form of sulphide.[28] Morin and " eriochromcyanin R. conc." are almost as sensitive reagents for aluminium as sodium alizarinsulphonate,[29] the reaction of which with many

[18] J. W. McBain, (Miss) M. E. Laing, and O. E. Clark, *J. Gen. Physiol.*, 1929, **12**, 695; *A.*, 899.

[19] J. Eisenbrand, *Pharm.-Ztg.*, 1929, **74**, 249; *A.*, 528.

[20] G. Gutzeit, *Helv. Chim. Acta*, 1929, **12**, 713, 829; *A.*, 898, 1254; P. Agostini, *Ann. Chim. Appl.*, 1929, **19**, 164; *A.*, 785; K. Heller and P. Krumholz, *Mikrochem.*, 1929, **7**, 213; *A.*, 900.

[21] A. Martini, *Anal. Asoc. Quím. Argentina*, 1928, **16**, 117; *Mikrochem.*, 1928, **6**, 152; *A.*, 164.

[22] *Idem, ibid.*, 1929, **7**, 30; *A.*, 287.

[23] I. M. Korenman, *Pharm. Zentr.*, 1929, **70**, 1; *A.*, 286.

[24] A. Martini, *Mikrochem.*, 1929, **7**, 236; *A.*, 898; S. Amberg, J. Landsbury, and F. Sawyer, *J. Amer. Chem. Soc.*, 1928, **50**, 2630; *A.*, 1928, 1347.

[25] L. Szebellédy, *Z. anal. Chem.*, 1928, **75**, 165; *A.*, 1928, 1347; H. W. van Urk, *ibid.*, 1929, **77**, 39; *A.*, 670.

[26] L. Szebellédy, *ibid.*, 1928, **75**, 167; *A.*, 1928, 1347.

[27] H. W. van Urk, *Chem. Weekblad*, 1928, **25**, 703; *A.*, 164.

[28] E. Grünsteidl, *Z. anal. Chem.*, 1929, **77**, 283; *A.*, 899.

[29] E. Eegriwe, *ibid.*, 1929, **76**, 438; *A.*, 531.

metals has been investigated.[30] The microchemical detection of lead [31] and of zinc, molybdenum, vanadium, and silver is described.[32] Polysulphide may be used to replace thiocyanate in Spacu's reaction for copper; [33] dimethylaminobenzylidenerhodanine in alcoholic solution forms a sensitive reagent for cuprous ion.[34]

Oxamide is less sensitive than dimethylglyoxime as a reagent for nickel; [35] the influence of various metals in the detection of cobalt with cyanate has been investigated.[36]

The diphenylcarbazide test for magnesium has been applied to silicates; [37] the reactions of magnesium salts with *op*-dihydroxy-azo-*p*-nitrobenzene [38] and various bisazo-dyes have been noted.[39]

Moderate amounts of lithium, rubidium, cæsium, and magnesium do not interfere with the detection of potassium by means of zirconium sulphate.[40] Sodium may be detected by precipitation as the triple acetate with uranium and cobalt [41] and microscopically by reaction with potassium antimonate.[42] A solution of sodium chromate and uranyl nitrate forms a sensitive reagent for potassium, rubidium, and chromium.[43] A scheme for the detection of alkali metals in mixtures with most of the commoner metals is described.[44]

Tables are given of the reactions of molybdates, nitrophospho-molybdates, tungstates, and phosphotungstates with many metal salts.[45] The identification of vanadium and cerium by means of hydrogen peroxide have been investigated, the interfering effect of molybdenum being suppressed by addition of boric acid.[46] Photo-

[30] F. G. Germuth and C. Mitchell, *Amer. J. Pharm.*, 1929, **101**, 46; *A.*, 286.

[31] G. Denigès, *Bull. Soc. chim.*, 1929, [iv], **45**, 678; *A.*, 1258.

[32] A. Martini, *Mikrochem.*, 1929, **7**, 231; *A.*, 900.

[33] A. J. Folcini, *Rev. Centr. Est. Farm. Bioquim.*, 1928, **17**, 305; *A.*, 1031.

[34] O. Funakoshi, *Mem. Coll. Sci. Kyoto*, 1929, **12**, 155; *A.*, 901; refer F. Feigl, *Z. anal. Chem.*, 1928, **74**, 380; *A.*, 1928, 1108; K. Heller and P. Krumholz, see ref. (20).

[35] J. Liška, *Chem. Listy*, 1929, **23**, 402; *A.*, 1260.

[36] B. J. F. Dorrington and A. M. Ward, *Analyst*, 1929, **54**, 327; *A.*, 901.

[37] H. Leitmeier and F. Feigl, *Tsch. Min. Petr. Mitt.*, 1928, **29**, 323; *A.*, 669; refer F. Feigl, *Z. anal. Chem.*, 1927, **72**, 113; *A.*, 1927, 1161.

[38] W. L. Ruigh, *J. Amer. Chem. Soc.*, 1929, **51**, 1456; *A.*, 783; refer Suitsu and Okuma, *J. Soc. Chem. Ind. Japan*, 1926, **29**, 132.

[39] E. Eegriwe, *Z. anal. Chem.*, 1929, **76**, 354; *A.*, 530.

[40] R. D. Reed and J. R. Withrow, *J. Amer. Chem. Soc.*, 1929, **51**, 1062; *A.*, 668; refer *idem, ibid.*, 1928, **50**, 1515, 2985; *A.*, 1928, 858; 1929, 165.

[41] E. R. Caley, *ibid.*, 1929, **51**, 1965; *A.*, 1031.

[42] W. Böttger, *Mikrochem.*, 1929, Pregl Fest., 14; *A.*, 1257.

[43] T. Gaspar y Arnal, *Anal. Fis. Quím.*, 1928, **26**, 184; *A.*, 1928, 1347.

[44] N. A. Tananaev, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 815; *A.*, 1257; *Z. anorg. Chem.*, 1929, **180**, 75; *A.*, 668.

[45] T. Gaspar y Arnal, *Anal. Fis. Quím.*, 1928, **26**, 435; *A.*, 417.

[46] J. Lukas and A. Jilek, *Chem. Listy*, 1929, **23**, 417; *A.*, 1260; *Z. anal. Chem.*, 1929, **76**, 348; *A.*, 532.

micrographs are produced for a number of crystalline derivatives of thallium [47] and a drop test for thallium is described.[48]

Microchemical tests for thiocyanate, fluoride, borate, chromate, and silica are described.[49] Improvements have been made in the molybdate-benzidine test for phosphate,[50] for which a solution of antimony trichloride and sodium molybdate also furnishes a sensitive reagent.[51] The reaction with mannitol has been applied to the detection of boric acid in the presence of most of the commoner anions and kations.[52]

The solution of zinc ethyl in pyridine forms a delicate reagent for the presence of active hydrogen in organic compounds.[53] Three tests for nitrites depend on coupling with aromatic amines.[54] Tri-, tetra-, and penta-thionates, but not dithionates or sulphites, catalyse the reaction between iodine and sodium azide.[55] Cerous and nickel nitrates are applied to a scheme for the qualitative analysis of mixtures of ferro- and ferri-cyanide and thiocyanate.[56] A molybdate-stannite reagent is used for the detection of traces of soluble silicate.[57] Tests for the differentiation of chloroamine from hypochlorite [58] and from free chlorine [59] are described, as also sensitive reactions for fluoride,[60] bromide, and iodide.[61]

Quantitative.—A universal indicator giving the spectrum colours has been developed.[62] The colorimetric determination of p_H by means of indicators and associated topics have been extensively

[47] A. J. Steenhauer, *Mikrochem.*, 1929, Pregl Fest., 315; *A.*, 1259.

[48] N. A. Tananaev and G. A. Pantschenko, *Ukraine Chem. J.*, 1929, **4**, 121; *A.*, 1032.

[49] F. Feigl, *Mikrochem.*, 1929, **7**, 10; *A.*, 284; F. Feigl and P. Krumholz, *ibid.*, 1929, Pregl Fest., 77; *A.*, 1255; *idem, Ber.*, 1929, **62**, [*B*], 1138; *A.*, 783.

[50] F. Feigl, *Z. anal. Chem.*, 1929, **77**, 299; *A.*, 900; H. Leitmeier, *Mikrochem.*, 1928, **6**, 144; *A.*, 162; refer F. Feigl, *Z. anal. Chem.*, 1928, **74**, 386; *A.*, 1928, 1107.

[51] T. Gaspar y Arnal, *Anal. Fis. Quim.*, 1928, **26**, 181; *A.*, 1928, 1346.

[52] A. S. Dodd, *Analyst*, 1929, **54**, 282; *A.*, 668.

[53] F. Haurowitz, *Mikrochem.*, 1929, **7**, 88; *A.*, 283.

[54] C. Goroncy, *Deut. Z. ges. gerichtl. Med.*, 1928, **11**, 482; *A.*, 667; W. Vaubel, *Chem.-Ztg.*, 1928, **52**, 842; *A.*, 1928, 1346; N. M. Ronshina, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 897; *A.*, 1256.

[55] L. Metz, *Z. anal. Chem.*, 1929, **76**, 347; *A.*, 529; refer F. Feigl, *ibid.*, 1928, **74**, 369; *A.*, 1928, 1106.

[56] P. C. Banerjee, *J. Indian Chem. Soc.*, 1929, **6**, 259; *A.*, 785.

[57] F. Oberhauser and J. Schormüller, *Z. anorg. Chem.*, 1929, **178**, 381; *A.*, 414.

[58] H. W. van Urk, *Chem. Weekblad*, 1929, **26**, 9; *A.*, 162.

[59] Besemann, *Chem.-Ztg.*, 1928, **52**, 826; *A.*, 1928, 1345.

[60] F. Pavelka, *Mikrochem.*, 1928, **6**, 149; *A.*, 162.

[61] E. Murmann, *Oesterr. Chem.-Ztg.*, 1929, **32**, 36; *A.*, 413.

[62] H. W. van Urk, *Pharm. Weekblad*, 1928, **65**, 1246; 1929, **66**, 157; *A.*, 162, 413.

investigated.[63] The uses have been investigated of yatren,[64] juice of the black mulberry,[65] 4-methylumbelliferone,[66] and a number of azo-compounds [67] as indicators, and of dimethylaminoazobenzene for the determination of the acidity of undissociated acids.[68]

Copper and copper sulphate,[69] potassium permanganate,[70] and cupric oxide [71] have been examined as standards in iodometry, and also the conditions favouring the stability of ferrous sulphate [72] and ceric sulphate [73] solutions. The latter substance has been applied to a number of different determinations,[74] as also have acid iodate solutions, of which the excess, together with the liberated iodine, is titrated with a stabilised potassium hydrogen sulphite solution.[75] Permanganate titrations have been made on the micro-scale,[76] and several analytical applications of sodium hyposulphite [77] and of mercuric nitrate [78] have been developed.

The temperature range between which a number of metallic sulphates are stable has been examined from an analytical standpoint, with the result that temperatures applicable to the satisfactory weighing of the sulphates are now made available.[79] The rapid

[63] E. Oeman, *Papier-Fabr.*, 1929, **27**, 27; *A.*, 162; F. C. Thompson and W. R. Atkin, *J. Soc. Leather-Trades Chem.*, 1929, **13**, 297; *A.*, 1158; J. Eisenbrand, *Pharm.-Ztg.*, 1929, **74**, 989, 1009, 1287; *A.*, 1157, 1255; A. Thiel and W. Springemann, *Z. anorg. Chem.*, 1928, **176**, 64, 112; *A.*, 41; F. R. McCrumb and W. R. Kenny, *J. Amer. Chem. Soc.*, 1929, **51**, 1458; *A.*, 782; H. Ruoss, *Z. anal. Chem.*, 1929, **77**, 175; *A.*, 782; A. Thiel, *Z. Elektrochem.*, 1929, **35**, 266; *A.*, 782; J. W. McBain, (Miss) M. E. Laing, and O. E. Clark, *J. Gen. Physiol.*, 1929, **12**, 695; *A.*, 899; I. M. Kolthoff, *J. Physical Chem.*, 1928, **32**, 1820; *A.*, 161; E. H. Fawcett and S. F. Acree, *J. Bact.*, 1929, **17**, 163; *A.*, 1255; C. E. Davis and H. M. Salisbury, *Ind. Eng. Chem.* [*Anal.*], 1929, **1**, 92; *A.*, 666; F. R. McCrumb and W. R. Kenny, *ibid.*, p. 44; *A.*, 413; D. H. Cameron, *J. Amer. Leather Chem. Assoc.*, 1929, **24**, 76; *A.*, 413.

[64] H. W. van Urk, *Z. anal. Chem.*, 1929, **77**, 12; *A.*, 666.

[65] L. Mosendz, *ibid.*, p. 37; *A.*, 666.

[66] C. Bülow and W. Dick, *ibid.*, 1928, **75**, 81; *A.*, 1928, 1345.

[67] N. A. Zaitzev, *J. Chem. Ind. Moscow*, 1928, **5**, 722; *A.*, 1029.

[68] A. Hantzsch and W. Voigt, *Ber.*, 1929, **62**, [*B*], 975; *A.*, 666.

[69] S. Popov, (Miss) M. Jones, C. Tucker, and W. W. Becker, *J. Amer. Chem. Soc.*, 1929, **51**, 1299; *A.*, 784.

[70] S. Popov and A. H. Kunz, *ibid.*, p. 1307; *A.*, 784.

[71] T. F. Buehrer and C. M. Mason, *Ind. Eng. Chem.* [*Anal.*], 1929, **1**, 68; *A.*, 669.

[72] J. A. N. Friend and E. G. K. Pritchett, *J.*, 1928, 3227; *A.*, 165.

[73] H. H. Willard and P. Young, *J. Amer. Chem. Soc.* 1929, **51**, 149; *A.*, 287.

[74] A. J. Berry, *Analyst*, 1929, **54**, 461; *A.*, 1159.

[75] A. Schwicker, *Z. anal. Chem.*, 1929, **77**, 161; *A.*, 782.

[76] J. Mika, *ibid.*, **78**, 268; *A.*, 1260.

[77] B. S. Evans, *Analyst*, 1929, **54**, 395; *A.*, 1030.

[78] E. Votoček and J. Kotrba, *J. Czech. Chem. Comm.*, 1929, **1**, 165; *A.*, 529.

[79] A. A. Guntz and J. Barbier, *Chim. et Ind.*, 1929, **21**, 711; *A.*, 668.

methods of preparing precipitates for weighing developed in connexion with, for example, copper pyridine thiocyanate, can be successfully applied to those obtained by the classical methods with considerable saving of time, e.g., silver halides, barium sulphate, calcium oxalate, nickel dimethylglyoxime.[80]

Indirect methods for the analysis of elements difficult to separate are discussed,[81] and also the influence of time of outflow and drainage on burette measurements.[82] For accurate micro-volumetric work, the weight burette is recommended,[83] and a description is given of the application of micro-analytical methods to technical problems.[84]

The apparatus for the determination of water by distillation with immiscible liquids has been modified in various ways in order to obviate the inaccuracies due to water sticking to the sides of the glass.[85]

The determination of small quantities of mercury has attracted much attention, several methods [86] having been investigated in addition to that described on p. 186; volumetric methods for larger quantities have also been investigated.[87] The hydrogenation process has been applied to the determination of cadmium as such in both organic and inorganic compounds.[88]

The presence of various enolic compounds and organic acids (excepting sulphinic acids) does not interfere with the iodometric determination of copper.[89] Small amounts of this element may be determined by a colorimetric process with dimethylglyoxime [90] or gravimetrically, not only as the pyridine thiocyanate already mentioned (p. 186), but also with dibromo-8-hydroxyquinoline,[91]

[80] J. Dick, Z. anal. Chem., 1929, **77**, 352; A., 901.

[81] O. Liesche, Z. angew. Chem., 1928, **41**, 1156; A., 1928, 1345.

[82] J. Lindner and F. Haslwanter, ibid., 1929, **42**, 821; A., 1033.

[83] B. Ormont, Z. anal. Chem., 1928, **75**, 209; A., 41.

[84] R. Lucas and F. Grassner, Mikrochem., 1928, **6**, 116; A., 161.

[85] W. Boller, Chem.-Ztg., 1928, **52**, 721; 1929, **53**, 70; A., 528; F. Friedrichs, ibid., p. 287; A., 667; J. Pritzker and R. Jungkunz, ibid., p. 603; A., 1029.

[86] R. Thilenius and R. Winzer, Z. angew. Chem., 1929, **42**, 284; A., 531; A. Stock and W. Zimmermann, ibid., p. 429; A., 784; J. Bodnár, ibid., p. 826; A., 1032; Friederich and Buhr, Süddeut. Apoth.-Ztg., 1928, **68**, 702; A., 784; E. H. Vogelenzang, Pharm. Weekblad, 1929, **66**, 65; A., 416.

[87] M. L. Colombier, J. Pharm. Chim., 1929, [viii], **10**, 15; A., 1032; H. B. Dunnicliff and H. D. Suri, Analyst, 1929, **54**, 405; A., 1031.

[88] H. ter Meulen and (Mlle.) H. J. Ravenswaay, Rec. trav. chim., 1929, **48**, 198; A., 285.

[89] M. I. Uschakov, J. Russ. Phys. Chem. Soc., 1928, **60**, 1151; Z. anal. Chem., 1928, **75**, 228; A., 1928, 1347.

[90] S. G. Clarke and B. Jones, Analyst, 1929, **54**, 333; A., 900.

[91] L. W. Haase, Z. anal. Chem., 1929, **78**, 113; A., 1159.

whilst " oxine " itself may be used for lead provided the quantity present is not too small.[92]

Bismuth is separated from lead by precipitation as basic nitrate with freshly prepared mercuric oxide [93] or by precipitation with cinchonine.[94]   Modifications and developments of the iodide method for the determination of small quantities of bismuth are described.[95]

A volumetric process for determining arsenic in organic and inorganic compounds in the presence of halogens and certain heavy metals is described [96] as well as the determination of arsine by two titrimetric methods.[97]   Finely divided antimony is found to be soluble in distilled water in the presence of oxygen.[98]   An improved form of the electrolytic Marsh apparatus has been applied to antimony.[99]   Small amounts of antimony are retained by the lead sulphate obtained by diluting the solution of lead–antimony alloys in sulphuric acid.[1]   A procedure for the preparation of antimony-free arsenious oxide is applied to the approximate determination of minute amounts of antimony in arsenious oxide.[2]   Reduction of stannic to stannous salts in acid media prior to titration with chloroamine or iodine is effected by electrolytic iron foil [3] or iron nails.[4]

Potassium cyanate is used for separations of metals of the third analytical group.[5]   8-Hydroxyquinoline has been applied to the micro-determination of aluminium,[6] and this reagent also serves to separate this metal from phosphate and various other elements which are normally coprecipitated by ammonia ; [7] the conditions necessary

[92] V. Marsson and L. W. Haase, *Chem.-Ztg.*, 1928, **52**, 993 ; *A.*, 164.

[93] H. Blumenthal, *Z. anal. Chem.*, 1929, **78**, 206 ; *A.*, 1258.

[94] Frick and Engemann, *Chem.-Ztg.*, 1929, **53**, 601 ; *A.*, 1033.

[95] *Idem, ibid.*, p. 505 ; *A.*, 1033 ; P. Dumont and M. Bouillenne, *Compt. rend. Soc. biol.*, 1928, **99**, 1247 ; *A.*, 1033 ; J. Straub, *Z. anal. Chem.*, 1929, **76**, 108 ; *A.*, 287.

[96] E. Schulek and P. von Villecz, *ibid.*, p. 81 ; *Ber. Ungar. pharm. Ges.*, 1928, **4**, 313 ; *A.*, 285, 668.

[97] H. Kubina, *Z. anal. Chem.*, 1929, **76**, 39 ; *A.*, 163.

[98] S. G. Clarke, *Analyst*, 1929, **54**, 99 ; *A.*, 417 ; J. Grant, *ibid.*, p. 227 ; *A.*, 639.

[99] *Idem, ibid.*, 1928, **53**, 626 ; *A.*, 165.

[1] A. Vasiliev and H. Stutzer, *Z. anal. Chem.*, 1929, **78**, 97 ; *A.*, 1159.

[2] C. W. Foulk and P. G. Horton, *J. Amer. Chem. Soc.*, 1929, **51**, 2416 ; *A.*, 1160.

[3] E. Rupp and F. Lewy, *Z. anal. Chem.*, 1929, **77**, 1 ; *A.*, 671.

[4] H. Wolf and R. Heilingötter, *Chem.-Ztg.*, 1929, **53**, 683 ; *A.*, 1160.

[5] R. Ripan, *Bul. Soc. Stiinte Cluj*, 1928, **4**, 57, 104 ; *A.*, 43.

[6] A. Benedetti-Pichler, *Mikrochem.*, 1929, Pregl Fest., 6 ; *A.*, 1259.

[7] G. E. F. Lundell and H. B. Knowles, *Bur. Stand. J. Res.*, 1929, **3**, 91 ; *A.*, 1260.

for precipitation of iron, manganese, nickel, and cobalt by this reagent have also been investigated.[8]   The complete simultaneous precipitation of iron and phosphoric acid is possible only when the ratio of iron to phosphorus is greater than two.[9]   Errors in the iodometric titration of iron have been traced to the presence of copper or of iron as oxide or colloidal hydroxide.[10]   The mechanism and limitations of the "molybdomanganimetry" of iron salts have been investigated.[11]   Ferric iron is quantitatively reduced by metallic copper in boiling sulphuric acid solution; uranyl salts are similarly reduced.[12]   The triphenylmethane dyes erioglaucin A or erio-green B can be used as indicators in the permanganate titration of iron or ferrocyanide.[13]

Sodium chloride interferes very seriously with the precipitation of zinc as sulphide [14] and as ammonium phosphate; [15] zinc may be completely separated from iron, aluminium, chromium, nickel, cobalt, and manganese by precipitation from faintly acid solutions in prescribed conditions.[16]   The colorimetric determination of manganese in the presence of silica has been examined and the precautions necessary for accurate determination described; [17] other volumetric methods for manganese have been investigated,[18] and also those for cobalt.[19]

A separation of strontium from barium depends on the different solubilities of the bromides in *iso*butyl alcohol,[20] and the microchemical separation of barium from calcium as chromate has been investigated.[21]   Small amounts of magnesium may be determined

[8] R. Berg, *Z. anal. Chem.*, 1929, **76**, 191; *A.*, 286.

[9] E. Angelescu and C. Bălănescu, *Kolloid.-Z.*, 1929, **47**, 207; *A.*, 532.

[10] E. C. Grey, *J.*, 1929, 35; *A.*, 286; see also E. H. Swift, *J. Amer. Chem. Soc.*, 1929, **51**, 2682; *A.*, 1260.

[11] P. Fleury and J. Marque, *J. Pharm. Chim.*, 1929, [viii], **9**, 479; *A.*, 784.

[12] G. Scagliarini and P. Pratesi, *Ann. Chim. Appl.*, 1929, **19**, 85; *A.*, 532.

[13] J. Knop and O. Kubelkova, *Chem. Listy*, 1929, **23**, 366, 399; J. Knop, *Z. anal. Chem.*, 1929, **77**, 111, 125; *A.*, 670.

[14] L. Dede, *Ber.*, 1928, **61**, [*B*], 2248; *A.*, 43.

[15] *Idem, ibid.*, p. 2463; *A.*, 164.

[16] J. Majdel, *Z. anal. Chem.*, 1929, **76**, 204; *A.*, 285; refer *Arhiv Hemiju*, 1928, **2**, 127; *A.*, 1928, 859.

[17] C. Newcomb, *Analyst*, 1928, **53**, 644; *A.*, 164.

[18] R. Lang and F. Kurtz, *Z. anorg. Chem.*, 1929, **181**, 111; *A.*, 1032; B. Reinitzer and F. Hoffmann, *Z. anal. Chem.*, 1929, **77**, 407; *A.*, 1032; J. Teletov and (Mme.) N. Andronikov, *Bull. Soc. chim.*, 1929, [iv], **45**, 674; *A.*, 1260.

[19] V. Cuvelier, *Natuurwetensch. Tijds.*, 1929, **11**, 123; *A.*, 1032; J. Gillis and V. Cuvelier, *ibid.*, p. 20; *A.*, 416; G. A. Barbieri, *Atti R. Accad. Lincei*, 1928, [vi], **8**, 405; *A.*, 416.

[20] L. Szebellédy, *Z. anal. Chem.*, 1929, **78**, 198; *A.*, 1258.

[21] R. Strebinger, *Mikrochem.*, 1929, **7**, 100; *A.*, 285.

gravimetrically with " oxine " [22] or colorimetrically with 1 : 2 : 5 : 8-tetrahydroxyanthraquinone.[23]

Given certain precautions, neglected by previous workers, sodium can be quantitatively determined as the triple magnesium uranyl acetate.[24]   Bromides may advantageously replace chlorides in the Lawrence Smith and Berzelius alkali determinations.[25]   Other investigations on the alkali metals have also been made.[26]

A simple volumetric determination of silver in the presence of halides and cyanides has been described,[27] and also a process, gravimetric or volumetric, involving the use of mercuric cyanide.[28] The analytical chemistry of gallium has been investigated; [29] " cupferron " is a useful reagent in this field.

Iron, aluminium, and copper can be removed from beryllium by means of "oxine"[30] and titanium from beryllium by p-chloroaniline.[31] Other analytical investigations of this element have been made.[32]

Tungsten can be separated from vanadium by precipitation as quinine arsenotungstate; [33]   the precipitation of tungsten by Berzelius's method [34] and various quantitative dry methods of examining tungsten compounds have been investigated.[35]   Methods for the gravimetric determination of vanadium are reviewed and expanded ; [36] and a volumetric process employing iodate is described.[37] Molybdenum is determined by means of permanganate following

[22] R. Strebinger and W. Reif, *Mikrochem.*, 1929, Pregl Fest., 319; *A.*, 1258.

[23] F. L. Hahn, *ibid.*, p. 127; *A.*, 1258.

[24] E. R. Caley with C. W. Foulk, *J. Amer. Chem. Soc.*, 1929, **51**, 1664; *A.*, 900.

[25] E. Spencer and K. B. Sen, *Analyst*, 1929, **54**, 224; *A.*, 530.

[26] F. Diaz de Rada, *Anal. Fis. Quim.*, 1929, **27**, 390; *A.*, 900; A. Thürmer, *Chem.-Ztg.*, 1928, **52**, 974; *A.*, 163; G. Jander and H. Faber, *Z. anorg. Chem.*, 1929, **181**, 189; *A.*, 1030; refer *idem, ibid.*, 1928, **173**, 225; *A.*, 1928, 980.

[27] H. Baines, *J.*, 1929, 2037; *A.*, 1257.

[28] F. Feigl and J. Tamchyna, *Ber.*, 1929, **62**, [*B*], 1897; *A.*, 1257.

[29] L. Moser and A. Brukl, *Monatsh.*, 1928, **50**, 181; 1929, **51**, 325; **52**, 253; *A.*, 1928, 1347; 1929, 670, 1260; R. Fricke and K. Meyring, *Z. anorg. Chem.*, 1928, **176**, 325; *A.*, 43.

[30] M. Niessner, *Z. anal. Chem.*, 1929, **76**, 135; *A.*, 285.

[31] B. E. Dixon, *Analyst*, 1929, **54**, 268; *A.*, 668.

[32] V. Čupr, *Z. anal. Chem.*, 1929, **76**, 173; *A.*, 285; H. Fischer, *Wiss. Veröff. Siemens-Konz.*, 1929, **8**, (1), 9; *A.*, 1031; L. Moser and F. List, *Monatsh.*, 1929, **51**, 181; *A.*, 415.

[33] A. Jílek and J. Lukas, *J. Czech. Chem. Comm.*, 1929, **1**, 263; *A.*, 785.

[34] V. Spitzin, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1229; *Z. anal. Chem.*, 1928, **75**, 433; *A.*, 165.

[35] V. Spitzin and L. Kaschtanov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1333; *Z. anal. Chem.*, 1928, **75**, 440; *A.*, 165.

[36] L. Moser and O. Brandl, *Monatsh.*, 1929, **51**, 169; *A.*, 415.

[37] E. H. Smith and R. W. Hoeppel, *J. Amer. Chem. Soc.*, 1929, **51**, 1366; *A.*, 785.

reduction with zinc ; [38] thallous salts may also be titrated in hydrochloric acid solution with this reagent if potassium chloride be added.[39]

The separation of osmium and ruthenium under various conditions is described ; [40] 6-nitroquinoline is a precipitant for palladium.[41] A detailed investigation has been made of the methods for the separation of lithium from sodium, potassium, and magnesium.[42] Further work is reported on the analytical chemistry of tantalum and niobium.[43]

The methods for determining ferrocyanide have been reviewed and preference is given to the permanganate titration.[44] In the titration with zinc,[45] diphenylamine can be used as internal indicator.[46] Modifications of the direct gravimetric method for carbon dioxide [47] have been made to eliminate interference by chloride and sulphide.[48] Thymolphthalein is recommended for titration of carbon dioxide with baryta.[49]

Volumetric processes for determination of sulphate have been investigated depending upon the use of benzidine acetate, the formation of yellow lead iodide and determining excess of barium by means of dichromate ; [50] methods applicable in the presence of fluorides are given.[51] Iodometric methods for various sulphur acids are described.[52] A rapid volumetric process for selenium, after precipitation in the usual way, has been devised.[53]

[38] J. Kassler, *Z. anal. Chem.*, 1928, **75**, 457 ; *A.*, 165.

[39] A. Jílek and J. Lukas, *Chem. Listy*, 1929, **23**, 124, 155 ; *J. Czech. Chem. Comm.*, 1929, **1**, 82 ; *A.*, 669, 783, 416.

[40] S. Saitō, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1929, **8**, 164 ; *A.*, 671.

[41] S. C. Ogburn, jun., and A. H. Riesmeyer, *J. Amer. Chem. Soc.*, 1928, **50**, 3018 ; *A.*, 166.

[42] L. Moser and K. Schutt, *Monatsh.*, 1929, **51**, 23 ; *A.*, 414.

[43] W. R. Schoeller and C. Jahn, *Analyst*, 1929, **54**, 320 ; *A.*, 902 ; W. R. Schoeller, *ibid.*, p. 453 ; *A.*, 1160 ; G. W. Sears, *J. Amer. Chem. Soc.*, 1929, **51**, 122 ; *A.*, 287.

[44] P. P. Budnikov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1159 ; *A.*, 1928, 1348.

[45] Azot Chemical Factory, Jaworzno, *Przemysł Chem.*, 1929, **13**, 65 ; *A.*, 416 ; H. Moll, *Chem. Weekblad*, 1928, **25**, 657 ; *A.*, 165.

[46] I. M. Kolthoff, *ibid.*, 1929, **26**, 298 ; *A.*, 785.

[47] R. C. Wiley, *J. Amer. Chem. Soc.*, 1929, **51**, 222 ; *A.*, 285.

[48] W. H. J. Vernon and L. Whitby, *J. Soc. Chem. Ind.*, 1928, **47**, 255T ; *B.*, 1928, 856 ; R. Chandelle, *Bull. Soc. chim. Belg.*, 1929, **38**, 248 ; *A.*, 1257.

[49] C. J. Schollenberger, *Ind. Eng. Chem.*, 1928, **20**, 1101 ; *A.*, 1928, 1346.

[50] G. Testoni, *Ann. Chim. Appl.*, 1928, **18**, 408 ; *A.*, 1928, 1345 ; Z. Mindalev, *Z. anal. Chem.*, 1928, **75**, 392 ; *A.*, 162 ; D. Kőszegi, *ibid.*, 1929, **77**, 203 ; *A.*, 782.

[51] H. Ginsberg with G. Holder, *Z. angew. Chem.*, 1929, **42**, 314 ; *A.*, 528.

[52] A. Schwicker, *Z. anal. Chem.*, 1929, **77**, 278 ; *A.*, 899 ; R. Wollak, *ibid.*, p. 401 ; *A.*, 1030 ; P. Szeberényi, *ibid.*, **78**, 36 ; *A.*, 1030.

[53] E. Benesch, *Chem.-Ztg.*, 1928, **52**, 878 ; *A.*, 42.

The presence of ashless filter paper hastens the volatilisation of silica when treated with hydrofluoric and sulphuric acids.[54]

Several investigators deal with colorimetric [55] and with gravimetric and volumetric [56] processes for phosphoric acid, and with the acidimetric [57] and iodometric [58] determination of phosphorous acid.

The volumetric methods for fluorides involving the formation of fluosilicate are described.[59] The determination of halogens in organic substances by electrolytic oxidation by the use of Gasparini's apparatus has been investigated.[60] Other papers deal with the determination of chloride,[61] bromide in sea water,[62] hypochlorite,[63] perchlorate,[64] and iodide.[65]

Dimethyl-α-naphthylamine gives a more permanent coloration than α-naphthylamine in nitrite determinations; [66] this anion may be separated by esterification.[67] Reduction methods for large [68] and small [69] quantities of nitrate are examined, and also gasometric methods for nitrous oxide.[70]

[54] T. Heczko, *Z. anal. Chem.*, 1929, **77**, 327; *A.*, 900.

[55] B. Vásárhelyi, *Mikrochem.*, 1929, Pregl Fest., 329; *A.*, 1256; E. Truog and A. H. Meyer, *Ind. Eng. Chem.* [*Anal.*], 1929, **1**, 136; *A.*, 1158; S. N. Rozanov, *Trans. Sci. Inst. Fertilisers, Moscow*, 1928, No. 55, 139; *A.*, 1158; C. Bordeianu, *Ann. sci. Univ. Jassy*, 1929, **15**, 372; *A.*, 782; A. Y. Levitzki, *Nauch. Agron. Zhur.*, 1927, **4**, 783; *A.*, 899.

[56] M. Ishibashi, *Mem. Coll. Sci. Kyoto*, 1929, **12**, 23, 39, 49, 135; *A.*, 529, 783; N. Krilenko, *Arhiv Hemiju*, 1928, **2**, 197; *A.*, 1928, 1346; W. Smith, *Quart. J. Pharm.*, 1929, **2**, 238; *A.*, 1159; M. Hegedüs, *Z. anal. Chem.*, 1928, **75**, 111; *A.*, 1928, 1346; K. Someya, *Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 1289; *A.*, 667; R. Dworzak and W. Reich-Rohrwig, *Z. anal. Chem.*, 1929, **77**, 14; *A.*, 667; W. Stollenwerk and A. Bäurle, *ibid.*, p. 81; *A.*, 667; Drachoussof and Douchy, *Chim. et Ind.*, 1928, **20**, 823; *A.*, 42.

[57] T. Miłobędzki and K. Boratyński, *Rocz. Chem.*, 1928, **8**, 554; *A.*, 414.

[58] A. Schwicker, *Z. anal. Chem.*, 1929, **78**, 103; *A.*, 1158.

[59] E. Bayle and L. Amy, *Compt. rend.*, 1929, **188**, 792; *A.*, 529; W. Siegel, *Z. angew. Chem.*, 1929, **42**, 856; *A.*, 1158.

[60] K. Heller, *Z. anal. Chem.*, 1929, **76**, 408; *A.*, 528; *idem*, with F. Hora and K. Willingshoffer, *ibid.*, **78**, 127; *A.*, 1158.

[61] R. K. McAlpine, *J. Amer. Chem. Soc.*, 1929, **51**, 1065; *A.*, 782; A. Frost, *Trans. Inst. Pure Chem. Reagents, Moscow*, 1927, No. 6, 35; *A.*, 1029; L. Moser with R. Miksch, *Mikrochem.*, 1929, Pregl Fest., 293; *A.*, 1255.

[62] A. I. Kogan, *Ukraine Chem. J.*, 1928, **3**, 131; *A.*, 1029.

[63] J. R. Lewis and R. F. Klockow, *J. Amer. Chem. Soc.*, 1928, **50**, 3243; *A.*, 162.

[64] O. S. Federova, *Z. anal. Chem.*, 1929, **78**, 749; *A.*, 1255.

[65] J. F. Reith, *Rec. trav. chim.*, 1929, **48**, 386; *A.*, 667.

[66] F. G. Germuth, *Ind. Eng. Chem.* [*Anal.*], 1929, **1**, 28; *A.*, 414.

[67] W. M. Fischer and A. Schmidt, *Z. anorg. Chem.*, 1929, **179**, 332; *A.*, 667.

[68] A. Seyewetz, *Bull. Soc. chim.*, 1929, [iv] **45**, 463; *A.*, 1030.

[69] B. G. Šimek, *Chem. Listy*, 1928, **22**, 353, 473; *A.*, 42.

[70] H. Menzel and W. Kretzschmar, *Z. angew Chem.*, 1929, **42**, 148; *A.*, 414.

Hydrogen peroxide, and indirectly lead dioxide, can be titrated with ceric sulphate.[71]

Organic Analysis.

Qualitative.—M. Wagenaar [72] describes microchemical reactions of (*a*) homatropine, (*b*) caffeine, (*c*) theobromine, (*d*) quinine, (*e*) quinidine, (*f*) cinchonine, (*g*) cinchonidine, (*h*) physostigmine, (*i*) piperine, and (*j*) sparteine; similar tests are described for morphine and allied substances [73] and for yohimbine [74]; also colour reactions are given for hydrastine and papaverine,[75] cantharidin,[76] bile acids,[77] gallic acid and tannin,[78] colchicine,[79] salvarsan and neosalvarsan,[80] adrenaline,[81] ergot alkaloids,[82] allantoin,[83] lævulose,[84] and *iso*butyl alcohol.[85]

5 : 5-Dimethyldihydroresorcinol ("methone" or "dimedon") yields characteristic condensation products with aldehydes; [86] 2 : 4-dinitrobenzaldehyde is a valuable reagent for the characterisation of amines and reactive methylene groups.[87] Thiolacetamide is useful for identifying arsinic acids [88] whilst methanesulphonyl chloride [89] and phenyl- and *o*-tolyl-thiocarbamides [90] are applied to the identification of amines. The *p*-nitrobenzyl ether esters of *o*-, *m*-, and *p*-hydroxybenzoic acids are described,[91] and some reactions

[71] N. H. Furman and J. H. Wallace, jun., *J. Amer. Chem. Soc.*, 1929, **51**, 1449; *A.*, 783.

[72] *Pharm. Weekblad*, 1928, **65**—(*a*) p. 1213, (*b*) p. 1334; 1929, **66**—(*c*) pp. 1, 131, (*d*) p. 177, (*e*) p. 197, (*f*) p. 253, (*g*) p. 261, (*h*) p. 381, (*i*) p. 405, (*j*) p. 809; *A.*, 79, 200, 460, 584, 584, 584, 584, 707, 829, 1319, respectively.

[73] L. Ekkert, *Pharm. Zentr.*, 1929, **70**, 165; *A.*, 584.

[74] G. Denigès, *Mikrochem.*, 1928, **6**, 113; *A.*, 201.

[75] C. A. Rojahn and F. Struffmann, *Pharm. Zentr.*, 1929, **70**, 277; *A.*, 829.

[76] H. W. van Urk, *Pharm. Weekblad*, 1929, **66**, 313; *A.*, 702.

[77] L. Cuny, *J. Pharm. Chim.*, 1928, [viii], **8**, 358; *A.*, 1928, 1389; *Compt. rend. Soc. Biol.* 1928, **99**, 613; *A.*, 699.

[78] S. A. Celsi, *Rev. Centr. Est. Farm. Bioquim.*, 1928, **16**, 642; *A.*, 86.

[79] L. Ekkert, *Pharm. Zentr.*, 1928, **69**, 662; *A.*, 86.

[80] H. W. van Urk, *Pharm. Weekblad*, 1929, **66**, 297; *A.*, 585.

[81] A. Orrù, *Ann. Chim. Appl.*, 1929, **19**, 239; *A.*, 1093.

[82] H. W. van Urk, *Pharm. Weekblad*, 1929, **66**, 473; *A.*, 832.

[83] R. Fosse and (Mlle.) V. Bossuyt, *Compt. rend.*, 1929, **188**, 106; *A.*, 196.

[84] L. Ekkert, *Pharm. Zentr.*, 1928, **69**, 805; *A.*, 174.

[85] A. Kutzlnigg, *Z. anal. Chem.*, 1929, **77**, 349; *A.*, 948.

[86] D. Vorländer, *ibid.*, p. 241; *A.*, 924; G. Klein and H. Linser, *Mikrochem.*, 1929, Pregl Fest., 204; *A.*, 1292.

[87] G. M. Bennett and W. L. C. Pratt, *J.*, 1929, 1465; *A.*, 1070.

[88] H. J. Barber, *ibid.*, p. 1024; *A.*, 833.

[89] C. S. Marvel and J. P. Belsley, *J. Amer. Chem. Soc.*, 1929, **51**, 1272; *A.*, 684.

[90] T. Otterbacher and F. C. Whitmore, *ibid.*, p. 1909; *A.*, 922.

[91] F. F. Blicke and F. D. Smith, *ibid.*, p. 1947; *A.*, 926.

of primary arsines,[92] and condensation products of p-aminoazobenzene with higher fatty acids.[93]

Quantatitive.—Investigations on the elementary analysis of organic compounds may be reviewed under the following heads : carbon and hydrogen,[94] nitrogen,[95] halogens generally,[96] and iodine in particular, especially when present in small amount,[97] sulphur,[98] phosphorus and arsenic,[99] antimony,[1] tin,[2] mercury,[3] selenium, and tellurium.[4]

Directions are given for the micro-determination of the acetyl value [5] and of the methylimino-,[6] methoxyl, and ethoxyl groups.[7]

A method for determining formaldehyde is based upon condensation with potassium cyanide to form the potassium compound of hydroxyacetonitrile ; [8]   " methone " (5 : 5-dimethyldihydro-

[92] S. S. Nametkin and V. Nekrassov, *Z. anal. Chem.*, 1929, **77**, 285; *A.*, 949.

[93] H. H. Escher, *Helv. Chim. Acta*, 1929, **12**, 27; *A.*, 293.

[94] S. Avery, *Ind. Eng. Chem.*, 1928, **20**, 1232; *A.*, 85: A. Boivin, *Compt. rend., Soc. Biol.*, 1929, **100**, 502: *A.*, 1323; *Compt. rend.*, 1928, **187**, 1076; *A.*, 204; F. Hernler, *Mikrochem.*, 1929, Pregl Fest., 140; *A.*, 1323; W. M. Lauer and F. J. Dobrovolny, *ibid.*, p. 243; *A.*, 1323; F. Böck and K. Beaucourt, *ibid.*, 1928, **6**, 133; *A.*, 204; M. Nicloux, *Bull. Soc. Chim. biol.*, 1928, **10**, 1271; *A.*, 204; R. Goubau, *Bull. Soc. chim. Belg.*, 1928, **37**, 335; *A.*, 42; D. Batescu, *Ber.*, 1928, **61**, [*B*], 2336; *A.*, 42.

[95] F. Halla, *Mikrochem.*, 1929, **7**, 202; *A.*, 899; W. M. Lauer and C. J. Sunde, *ibid.*, Pregl Fest., p. 235; *A.*, 1323; F. Hernler, *ibid.*, p. 154 : *A.*, 1323; I. Marek with M. Krajčinovič and G. Zaljesov, *Bull. Soc. chim.*, 1929, [iv], **45**, 555; *Arhiv Hemiju*, 1928, **2**, 169; *A.*, 1928, 1346; S. Ōkido, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1929, **8**, 2; *A.*, 337; G. Wallerius, *Tekn. Tidsskr.*, 1928, **58**, Kemi, 33; *A.*, 85.

[96] W. Roman, *Biochem. Z.*, 1929, **207**, 416; *A.*, 713; F. Hein, K. Hoyer, and K. Klar, *Z. anal. Chem.*, 1928, **75**, 161; *A.*, 1928, 1389.

[97] J. Schwaibold, *ibid.*, 1929, **78**, 161; *A.*, 1256; *Chem.-Ztg.*, 1929, **53**, 22; *A.*, 337; J. F. Reith, *Chem. Weekblad*, 1929, **26**, 26; *A.*, 337; *Rec. trav. chim.*, 1929, **48**, 254; *A.*, 414; J. F. McClendon and R. E. Remington, *J. Amer. Chem. Soc.*, 1929, **51**, 394; *A.*, 413; G. Lunde, K. Closs, and J. Boë, *Mikrochem.*, 1929, Pregl Fest., 272; *A.*, 1323; T. Leipert, *ibid.*, p. 266; *A.*, 1323; E. I. van Itallie, *Pharm. Weekblad*, 1929, **66**, 629; *A.*, 1093.

[98] I. Marek, *Bull. Soc. chim.*, 1928, [iv], **43**, 1405; *A.*, 337; F. Hein, K. Hoyer, and K. Klar, *Z. anal. Chem.*, 1928. **75**, 161; *A.*, 1928, 1389; E. A. Smith and J. W. Bain, *Canadian Chem. Met.*, 1928, **12**, 287; *A.*, 1928, 1389; K. Heller, *Mikrochem.*, 1929, **7**, 208; *A.*, 948; A. Friedrich, *ibid.*, Pregl Fest., 91; *A.*, 1323.

[99] K. Heller, *Mikrochem.*, 1929, **7**, 208; *A.*, 948.

[1] S. Ghosh, *Indian J. Med. Res.*, 1929, **16**, 457; *A.*, 1188.

[2] H. Gilman and W. B. King, *J. Amer. Chem. Soc.*, 1929, **51**, 1213; *A.*, 713.

[3] F. Hernler, *Mikrochem.*, 1929, Pregl Fest., 154; *A.*, 1323.

[4] H. D. K. Drew and C. R. Porter, *J.*, 1929, 2091; *A.*, 1323.

[5] F. Pregl and A. Soltys, *Mikrochem.*, 1929, **7**, 1; *A.*, 337.

[6] A. Friedrich, *ibid.*, p. 195; *A.*, 949; P. Haas, *ibid.*, p. 69; *A.*, 337.

[7] A. Friedrich, *ibid.*, p. 185; *A.*, 948.

[8] F. Lippich, *Z. anal. Chem.*, 1929, **76**, 241, 255; *A.*, 460.

resorcinol) is applied quantitatively to formaldehyde and/or acet-aldehyde.[9] Silver nitrate is used as an absorbent for ethylene which is recovered by diminishing the pressure.[10] Quantitative methods for the following acids are described : hydrocyanic,[11] formic and acetic,[12] butyric,[13] pyruvic,[14] citric and tartaric,[15] lactic,[16] and amino-acids.[17]

The reaction between thiosemicarbazide and iodine has been investigated in acid and in alkaline solution,[18] while determination of the ammonia which is obtained together with hydrazine by hydro-lysis of semicarbazide is applied to the micro-analysis of ketones.[19] The solubility of the picrate interferes with the accuracy of the method of determining hexamethylenetetramine by means of this salt.[20]

Sugars and allied compounds continue to attract much attention.[21]

Methylene-blue is completely precipitated by picric acid.[22] Like the strychnine salt, brucine silicotungstate is of variable com-position.[23]

[9] D. Vorländer with C. Ihle and H. Volkholz, *Z. anal. Chem.*, 1929, **77**, 321 ; *A.*, 949.

[10] V. N. Morris, *J. Amer. Chem. Soc.*, 1929, **51**, 1460 ; *A.*, 948.

[11] W. P. Malitzky and M. T. Koslovsky, *Mikrochem.*, 1929, **7**, 94 ; *A.*, 337.

[12] P. Fuchs, *Z. anal. Chem.*, 1929, **78**, 125 ; *A.*, 1323.

[13] R. J. Allgeier, W. H. Peterson, and E. B. Fred, *J. Bact.*, 1929, **17**, 79 ; *A.*, 1093.

[14] B. H. R. Krishna and M. Sreenivasaya, *J. Indian Inst. Sci.*, 1929, **12A**, 41 ; *A.*, 677.

[15] F. Pirrone, *Riv. Ital. Ess. Prof.*, 1928, **10**, 101 ; *A.*, 836.

[16] E. Lehnartz, *Z. physiol. Chem.*, 1928, **179**, 1 ; *A.*, 48 ; T. E. Friedemann and A. I. Kendall, *J. Biol. Chem.*, 1929, **82**, 23 ; *A.*, 677.

[17] L. Rosenthaler, *Biochem. Z.*, 1929, **207**, 298 ; *A.*, 713 ; W. Grassmann and W. Heyde, *Z. physiol. Chem.*, 1929, **183**, 32 ; *A.*, 949.

[18] A. Gaffre, *J. Pharm. Chim.*, 1929, [viii], **9**, 19 ; *A.*, 302.

[19] R. P. Hobson, *J.*, 1929, 1384 ; *A.*, 949 ; S. Veibel, *ibid.*, p. 2423 ; refer *Bull. Soc. chim.*, 1927, **41**, 1410 ; *A.*, 1927, 1172.

[20] C. V. Bordeianu, *Ann. sci. Univ. Jassy*, 1929, **15**, 380 ; *A.*, 836.

[21] F. González and A. Gimeno, *Anal. Fis. Quim.*, 1929, **27**, 39 ; *A.*, 798 ; T. Fukai, *Bul. Ferm. Tokyo*, 1928, No. 100, 106 ; *A.*, 836 ; C. Kullgren and H. Tydén, *Handl. Ing. Vetenskaps-Akad. Stockholm*, 1929, No. 94 ; *A.*, 1278 ; P. Fleury and J. Marque, *Compt. rend.*, 1929, **188**, 1686 ; *A.*, 948 ; H. Elsner, *Ber.*, 1928, **61**, [*B*], 2364 ; *A.*, 50 ; J. Voicu and (Mlle.) V. Dumitrescu, *Bul. Soc. Chim. Románia*, 1929, **11**, 15 ; *A.*, 1189 ; A. A. Gabreëls and A. L. van Scherpenberg, *Chem. Weekblad*, 1929, **26**, 394 ; *A.*, 1045 ; W. Braun and B. Bleyer with W. Elhardt, *Z. anal. Chem.*, 1929, **76**, 1 ; *A.*, 205 ; A. B. Schach-keldian, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1517 ; *A.*, 298 ; R. Biazzo, *Ann. Chim. Appl.*, 1928, **18**, 447 ; *A.*, 85.

[22] M. François and (Mlle.) L. Seguin, *J. Pharm. Chim.*, 1929, [viii], **10**, 5 ; *A.*, 1084.

[23] B. Kljatschkina and M. Strugadski, *Arch. Pharm.*, 1929, **267**, 177 ; *A.*, 708.

Pyrazolones and aromatic sulphonarylamides can be titrated alkalimetrically.[24] The blue coloration formed by diphenylamine and ferric sulphate is applied to the determination of the former.[25] A process applicable to mixtures of anthraquinone with benzanthrone is described, the latter being first oxidised to anthraquinonecarboxylic acid.[26]

Physical Methods.

A number of examples of the use of radio-elements as indicators is described.[27] The theory of physical titration (*e.g.*, turbidimetric analysis) is discussed ; [28] many ordinary titrations can, when carried out in Dewar flasks, be followed thermometrically.[29] The addition of glycerol greatly augments the stability of the suspensions of barium sulphate obtained for nephelometric purposes.[30]

Much work has been carried out on spectrographic methods of analysis.[31] These have been applied in particular to the detection of lead in gold–copper–silver alloys,[32] to the determination of iridium, rhodium, and palladium in platinum,[33] detection of beryllium,[34] determination of strontium, barium, and cæsium in rocks and mineral waters,[35] of zinc in solution, and of molybdenum in steel.[36] The spectrophotometer is preferred to the colorimeter for the determination of aluminium by means of aluminon.[37]

Electrochemical Methods.

Electrolytic.—The separation of niobium and tantalum in tantalite by electrolytic hydrolysis is described,[38] and also the reduction of

[24] K. Heller and Z. Fleischhans, *J. pr. Chem.*, 1929, [ii], **123**, 146 ; *A.*, 1324.

[25] A. Thiel, *Z. Elektrochem.*, 1929, **35**, 274 ; *A.*, 836.

[26] P. I. Sokolov and L. Gurevich, *J. Chem. Ind. Moscow*, 1928, **5**, 308 ; *A.*, 205.

[27] F. Paneth, *Z. angew. Chem.*, 1929, **42**, 189 ; *A.*, 528 ; R. Ehrenberg, *Mikrochem.*, 1929, Pregl Fest., 61 ; *A.*, 1258.

[28] E. N. Gapon, *Ukraine Chem. J.*, 1929, **4**, 149 ; *A.*, 1254.

[29] C. Mayr and J. Fisch, *Z. anal. Chem.*, 1929, **76**, 418 ; *A.*, 528.

[30] J. Křepelka and A. Kalina, *Chem. Listy*, 1928, **22**, 545 ; *A.*, 163.

[31] T. Negresco, *J. Chim. physique*, 1928, **25**, 343, 363 ; *A.*, 161 ; C. C. Nitckie, *Ind. Eng. Chem. [Anal.]*, 1929, **1**, 1 ; *A.*, 412 ; H. Thurnwald and G. F. Hüttig, *Z. anal. Chem.*, 1929, **76**, 260 ; *A.*, 413 ; F. Gromann, *Z. anorg. Chem.*, 1929, **180**, 257 ; *A.*, 784.

[32] W. Gerlach and E. Schweitzer, *Z. anorg. Chem.*, 1929, **181**, 101 ; *A.*, 1031.

[33] *Idem, ibid.*, p. 103 ; *A.*, 1033.

[34] H. Fesefeldt, *Z. physikal. Chem.*, 1929, **140**, 254 ; *A.*, 530.

[35] F. Zambonini and V. Caglioti, *Atti R. Accad. Lincei*, 1928, [vi], **8**, 268 ; *A.*, 415.

[36] H. Thurnwald, *Z. anal. Chem.*, 1929, **76**, 335 ; *A.*, 530 ; W. Gerlach and E. Schweitzer, *ibid.*, **77**, 213 ; *A.*, 782.

[37] E. W. Schwartze and R. M. Hann, *Science*, 1929, **69**, 167 ; *A.*, 901.

[38] L. F. Yntema, *Amer. Electrochem. Soc.*, 1929, May ; *A.*, 671.

nitrates to ammonia by sodium amalgam produced by electrolysis.[39] A polarographic investigation with the dropping-mercury cathode of solutions of arsenious oxide in hydrochloric acid has been carried out.[40]

A modified electrolytic apparatus is described which permits of reducing the weight of platinum required,[41] as well as the use of mercury [42] and of Wood's metal as cathodes.[43] Results of numerous experiments on the separation of metals by Sand's method are given.[44] Electrolytic methods are described for the rapid determination of tin,[45] thallium,[46] bismuth,[47] cadmium and zinc,[48] and lead.[49]

Potentiometric.—Quinhydrone for analytical work should be free from iron salts.[50] Several modifications of apparatus have been described, mainly in the direction of simplification.[51]

Ceric sulphate has been used as a volumetric oxidising agent for chromium in the presence of certain other metals [52] and for ferrocyanide.[53] Reaction of this anion with gallium has been examined,[54] whilst ferricyanide in alkaline solution has been used for vanadium and hyposulphite,[55] arsenic, antimony, tin, and thallium.[56]

[39] M. Rabinovitsch and A. S. Fokin, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 315; *Z. Elektrochem.*, 1929, **35**, 18; *A.*, 284.

[40] K. Kačírková, *J. Czech. Chem. Comm.*, 1929, **1**, 477; *A.*, 1256.

[41] H. J. S. Sand, *Analyst*, 1929, **54**, 275; *A.*, 672.

[42] W. Moldenhauer with K. F. A. Ewald and O. Roth, *Z. angew. Chem.*, 1929, **42**, 331; *A.*, 531.

[43] H. A. J. Pieters, *Chem. Weekblad*, 1928, **25**, 706; *A.*, 161; compare H. Paweck and R. Weiner, *Z. anal. Chem.*, 1927, **72**, 225; *A.*, 1928, 143.

[44] N. Vensovitch, *Bull. Soc. chim. Belg.*, 1928, **37**, 353; *A.*, 286.

[45] J. Švéda and R. Uzel, *J. Czech. Chem. Comm.*, 1929, **1**, 203; *A.*, 671.

[46] A. Jílek and J. Lukas, *ibid.*, p. 417; *A.*, 1159.

[47] *Idem, ibid.*, p. 369; *A.*, 1033.

[48] E. Brennecke, *Z. anal. Chem.*, 1928, **75**, 321; *A.*, 164.

[49] H. Töpelmann, *J. pr. Chem.*, 1929, [ii], **121**, 289; *A.*, 669; A. Seiser, A. Necke, and H. Müller, *Z. anal. Chem.*, 1929, **42**, 96; *A.*, 286.

[50] M. Trénel and C. Bischoff, *Z. angew. Chem.*, 1929, **42**, 288; *A.*, 528.

[51] D. A. MacInnes and M. Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 1119; *A.*, 666; A. Uhl, *Z. anal. Chem.*, 1929, **77**, 280; *A.*, 899; I. I. Shukov and G. P. Avsejevitsch, *Z. Elektrochem.*, 1929, **35**, 349; *A.*, 899; T. Heczko, *Z. anal. Chem.*, 1928, **75**, 183; *A.*, 1928, 1345; B. Kamieński, *Bull. Acad. Polonaise*, 1928, **A**, 33; *A.*, 1928, 1345; L. Köhler, *Chem.-Ztg.*, 1929, **53**, 69; *A.*, 528; E. Müller and H. Kogert, *Z. anal. Chem.*, 1928, **75**, 235; *A.*, 42; H. H. Willard and A. W. Boldyreff, *J. Amer. Chem. Soc.*, 1929, **51**, 471; *A.*, 413; F. L. Hahn, *Z. anal. Chem.*, 1929, **76**, 146; *A.*, 283; L. Kahlenberg and A. C. Krueger, *Amer. Electrochem. Soc.*, Sept. 1929; *A.*, 1255; T. Callan and S. Horrobin, *J. Soc. Chem. Ind.*, 1928, **47**, 329T; *B.*, 154.

[52] H. H. Willard and P. Young, *J. Amer. Chem. Soc.*, 1929, **51**, 139; *A.*, 287.

[53] N. H. Furman and O. M. Evans, *ibid.*, p. 1128; *A.*, 670; K. Someya, *Z. anorg. Chem.*, 1929, **181**, 183; *A.*, 1032.

[54] S. Ato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, **10**, 1; *A.*, 416.

[55] C. del Fresno and L. Valdés, *Anal. Fis. Quim.*, 1929, **27**, 368; *A.*, 901; *Z. anorg. Chem.*, 1929, **188**, 251; *A.*, 1257.   [56] *Idem, ibid.*, p. 258; *A.*, 1257.

Silver and cadmium may be consecutively determined with bromide and ferrocyanide respectively.[57] Methods have been described for the determination of copper,[58] of small quantities of lead,[59] of chromic acid in presence of vanadic,[60] of iron,[61] manganese,[62] titanium,[63] gold and platinum,[64] osmium,[65] boric acid,[66] iodides,[67] iodomercurates,[68] and thence indirectly of morphine.[69]

Conductometric.—A visual method for carrying out conductometric titrations has been described [70] and applied to the rapid determination of sulphate in drinking water.[71] The neutralisation of phosphoric acid by sodium hydroxide has been investigated conductometrically.[72].

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[57] E. Müller and H. Hentschel, *Z. anal. Chem.*, 1928, **75**, 240; *A.*, 42.

[58] (Miss) M. E. Pring and J. F. Spencer, *Analyst*, 1929, **54**, 509, 576; *A.*, 1259.

[59] H. Millet, *Trans. Faraday Soc.*, 1929, **25**, 147; *A.*, 531.

[60] E. Zintl and P. Zaimis, *Z. Elektrochem.*, 1928, **34**, 714; *A.*, 1928, 1348.

[61] T. Heczko, *Z. anal. Chem.*, 1929, **78**, 247; *A.*, 1260; H. Brintzinger and W. Schieferdecker, *ibid.*, p. 110; *A.*, 1159; B. A. Soule, *J. Amer. Chem. Soc.*, 1929, **51**, 2117; *A.*, 1032.

[62] B. F. Brann and M. H. Clapp, *ibid.*, p. 39; *A.*, 286.

[63] H. Brintzinger and W. Schieferdecker, *Z. anal. Chem.*, 1929, **76**, 277; *A.*, 417.

[64] E. Müller and R. Bennewitz, *Z. anorg. Chem.*, 1929, **179**, 113; *A.*, 532.

[65] W. R. Crowell and H. D. Kirschman, *J. Amer. Chem. Soc.*, 1929, **51**, 175, 1695; *A.*, 287, 1029.

[66] I. V. Grebenschtschikov and T. A. Favorskaia, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 561; *A.*, 1030.

[67] O. Tomíček, *J. Czech. Chem. Comm.*, 1929, **1**, 443; *A.*, 1158.

[68] L. Maricq, *Bull. Soc. chim. Belg.*, 1929, **38**, 259; *A.*, 1259.

[69] *Idem, ibid.*, p. 265; *A.*, 1320.

[70] G. Jander and O. Pfundt, *Z. Elektrochem.*, 1929, **35**, 206; *A.*, 652.

[71] H. Fehn, G. Jander, and O. Pfundt, *Z. angew. Chem.*, 1929, **42**, 158; *B.*, 342.

[72] (Miss) J. C. Lanzing and L. J. van der Wolk, *Rec. trav. chim.*, 1929, **48**, 83; *A.*, 284.

BIOCHEMISTRY.

The Intake and Accumulation of Electrolytes by Plant Cells.

D. R. HOAGLAND and his co-workers in the laboratory of Plant Nutrition in California, whose researches on the fresh-water alga *Nitella* were discussed in earlier reports,[1] have published an interesting review which embodies a great deal of more recent work.[2] No striking advance is recorded, but they have obtained many further data to support their view that the intake of substances into living cells can be interpreted only in terms of ions, and not, as W. J. V. Osterhout and others suggest, in terms of undissociated molecules. They also insist that the accumulation of solutes in the vacuolar sap of plant cells, often to a concentration many times that of the surrounding medium, is dependent on energy exchanges, and cannot be explained by adsorption phenomena on the sap colloids,[3] which, in the case of *Nitella* sap, are more or less non-existent. The chemical or electrical reactions responsible for this output of energy must, it is admitted, take place in exceedingly thin layers of protoplasm, which must necessarily imply a high degree of heterogeneity in the protoplasmic system. The experimental evidence in support of this assumption was discussed in last year's Report.[4] In view of the large number of papers published in recent years on the permeability of artificial membranes it is interesting to note that, if Hoagland's views be correct, no artificial cell can imitate completely a living cell unless arrangements be made to supply energy in suitable form to the artificial system.

Fat Metabolism in the Plant.

During the past few years there has been a great increase in the interest displayed in the field of plant fats. Although much fundamental work remains to be done and is being done in the field of seed fats and oils, it is pleasing to note that the fatty substances of green plants, yeasts and bacteria representing more physiologically active tissues are beginning to receive attention.

Phosphatides.—The work of Schulze and his school on the seed phosphatides was inconclusive, in that preparations free from sugar were seldom obtained, and only through the similarity of the de-

[1] *Ann. Reports*, 1925, **22**, 313; 1926, **23**, 223.
[2] *Protoplasma*, 1929, **6**, 610.
[3] W. Stiles, *ibid.*, 1927, **5**, 577.   [4] *Ann. Reports*, 1928, **25**, 227.

composition products could the presence of true animal lecithin or kephalin be inferred.   P. A. Levene [5] has recently been able to obtain in bulk some commercial preparations of crude phosphatide from the soya bean.   By intensive fractionation he has obtained a pure preparation of lecithin which is free from sugar, a kephalin containing only 10% of its nitrogen in the non-amino- form, and products resembling animal cuorins (*i.e.*, with an N : P ratio of 1 : 2 ; which are now considered to be mixtures of decomposition products). Most of Levene's work has been recently substantiated by B. Rewald.[6]   This clear demonstration that the phosphatides of the seed do not differ from the well-known phosphatides found in the animal body makes their absence in the cabbage leaf, wherein their place is taken by calcium phosphatidate, the more remarkable,[7] and raises the question of the physiological relationship existing between the phosphatides of the seed and of the leaf.   Will a plant such as the soya bean, having lecithin and kephalin in its seed, have calcium phosphatidate in its leaves ?   Such an occurrence would be totally unexpected if we regarded the phosphatides in the usual way as essential constituents of the cell.   A. C. Chibnall and H. J. Channon suggest that the difference might be understood if the rôle of the two types of phosphatides were different either in their effects on permeability or as agents in the transport of fat, but obviously much further research into the distribution of the various phosphatides in seeds and green plants will be necessary before any such generalisation can be made.

Turning to the lower organisms, we find the same conflicting evidence.   G. G. Daubney and I. S. Maclean[8] show that the phosphatides of yeast consist of the usual mixture of lecithin and kephalin, which on hydrolysis gives rise to a larger proportion of unsaturated than saturated acids.   This low proportion of saturated acid is also found in the soya-bean phosphatides, and cabbage calcium phosphatidate, but the reverse is the case in the phosphatides of tubercle bacilli.   These have recently been examined in some detail by R. J. Anderson [9] and exhibit such unusual characters that they warrant more than a passing reference.   The acetone–ether insoluble fraction was found to consist of a wax (referred to later, p. 212) and a phosphatide.   The latter contained 0·40% of nitrogen, all of which can

    [5] P. A. Levene and Ida P. Rolf, *J. Biol. Chem.*, 1925, **62**, 759 ; 1926, **68**, 285 ; *A.*, 1925, i, 487 ; 1926, 982.

    [6] *Biochem. Z.*, 1929, **211**, 199 ; *A.*, 1347.

    [7] *Ann. Reports*, 1927, **24**, 230 ; A. C. Chibnall and H. J. Channon, *Biochem. J.*, 1929, **23**, 176 ; *A.*, 729.

    [8] *Biochem. J.*, 1927, **21**, 373.

    [9] *J. Biol. Chem.*, 1927, **74**, 537 ; 1929, **83**, 169, 505 ; *A.*, 1927, 1114 ; 1929, 1108, **1342.**

be distilled off as ammonia with alkali, and 2·14% of phosphorus and showed no reducing properties when an aqueous suspension was boiled with Fehling's solution.

An investigation of the products given by acid hydrolysis yielded 5·4% of glycerophosphoric acid, 13·8% of an unidentified sugar acid, 13·9% of glucose, 30·5% of palmitic acid, 12·8% of oleic acid, and 20·9% of a new liquid saturated fatty acid. The substance, if it is a chemical entity, which Anderson is not yet prepared to certify, is obviously more complex than any of the well-recognised phosphatides, and is especially interesting in that over 50% of it is made up of saturated fatty acids. The separation of the individual acids presented considerable difficulties, and the new liquid saturated acid, which Anderson calls phthioic acid, was obtained free from oleic acid only by hydrogenating the latter and removing the resulting stearic acid as ether-insoluble lead soap. Phthioic acid is a colourless liquid which sets to a white solid when cooled in ice-water and liquefies on warming to 10°. Its constitution is not yet determined, but it exhibits a specific rotation in alcoholic solution of + 1·5° (see p. 209).

This tubercle phosphatide has been found to have powerful pathogenetic properties. F. R. Sabin and C. A. Doan * observed that intraperitoneal injections of an aqueous suspension of the substance into normal rabbits caused a large increase in monocytes, epithelioid and giant cells and that the injections were followed by the development of massive typical tubercular tissue in the peritoneal cavity. Phthioic acid gives practically identical reactions, so that it is obvious that the active principle of the phosphatide is associated with this new interesting acid.

The above account of recent work shows that the concept of only three well-defined phosphatides, *viz.*, lecithin, kephalin, and sphingomyelin, which appeared sufficient to explain data derived from animal sources, may need modification when we come to consider the plant and micro-organisms. The lessons to be learnt from the " jecorin " and " cuorin " stories, however, can still be taught with advantage, for the phosphatide field is one which occasionally attracts biologists, and in no other is experience more essential. In the work [10] of V. Grafe, H. Cranner and their schools on the so-called diffusible water-soluble phosphatides of vegetable tissues, no attempt has been made to isolate these phosphatides in any state of purity ; indeed, their very existence has not yet been satisfactorily demonstrated : the work calls for no further comment.

Plant Glycerides.—Mention was made in another section of last

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* Quoted by R. J. Anderson (ref. 9).

[10] See F. C. Steward, *Biochem. J.,* 1928, **22**, 268 ; *A.,* 1928, 334.

year's Report [11] of the new methods employed by Hilditch and his co-workers to determine the structural composition of glycerides. Further work [12] has confirmed their earlier conclusion that there is a pronounced tendency to even distribution of the fatty acids throughout the glycerides of seed (kernel) fats as a class. If the molecular proportion of unsaturated to saturated acids in the whole fat exceeds about 1·6 to 1, the saturated acids are almost wholly present in the form of mixed glycerides : if the aforesaid molecular proportion is reversed, increasing amounts of fully saturated glycerides are found to be present, but in every case except one so far examined the mixed saturated–unsaturated glycerides present contain saturated and unsaturated acids in molecular ratios lying within the comparatively narrow limits of 1·3—1·6 to 1 : finally, when fully saturated glycerides are present in quantity, no simple triglyceride has been detected (even when one acid forms 30—50% of the whole of the saturated acids, e.g., lauric acid in coconut and palm-kernel fats or palmitic and stearic acids in cacao butter or illipé tallow) unless the composition of the saturated fatty acid is so simple that one acid is present in overwhelming excess (e.g., myristic acid in nutmeg butter, which contains a considerable proportion of trimyristin). In the case of non-seed plant fats, such as laurel fat, the glyceride structure is much more heterogeneous. Although the molecular proportions of saturated and unsaturated acids in the whole fat are approximately equal, the fat contains 26% of fully saturated triglycerides (mostly trilaurin) and the molecular ratio of the saturated to unsaturated acids in the mixed glycerides shows further that tri-unsaturated glycerides must be present in quantity. This work on the glycerides is enabling Hilditch slowly to accumulate data with respect to the distribution of fatty acids in the seed fats, but the evidence is still somewhat scanty and diffuse. Certain acids, such as oleic and linoleic, occur in fair to considerable proportions in most fats, but the four acids, lauric, myristic, erucic, and pitroselinic ($\Delta^{6:7}$-octadecenoic), stand out quite definitely in their nature and proportion in the respective cases of the four orders, *Palmæ*, *Myristiceæ*, *Cruciferæ*, and *Umbelliferæ*.[13]

Turning to the fats of green parts of the plant and of micro-organisms, we find the problem rendered far more difficult by the presence of considerable proportions of phosphatides and unsaponifiable material. Investigation of the fatty acids obtained after saponification of the acetone–ether soluble material from cabbage [14]

[11] *Ann. Reports*, 1928, **25**, 85.

[12] G. Collin and T. P. Hilditch, *Biochem. J.*, 1929 (in the press).

[13] T. P. Hilditch, *Proc. Roy. Soc.*, 1928, *B*, **103**, 111; *A.*, 1928, 1059; B. C. Christian and T. P. Hilditch, *Biochem. J.*, 1929, **23**, 327; *A.*, 855.

[14] A. C. Chibnall and H. J. Channon, *Biochem. J.*, 1927, **21**, 479; 1929, **23**, 176; *A.*, 1927, 799; 1929, 724.

showed that the fatty acids were very highly unsaturated (iodine value, over 200). The greater part consists of linoleic and linolenic acids (acids of higher degree of unsaturation were not found), with only small amounts of palmitic and stearic acids. Analysis of a similar fraction from yeast [15] showed an iodine value of 77, and the presence of oleic and linoleic acids. In both these cases the fatty acids from the glyceride fractions are more unsaturated than those from the corresponding phosphatide fractions, which is the reverse of that usually found in the animal body. Examination of the fatty acids from dried spinach leaves, without previous removal of phosphatides,[16] showed a mixture similar to that from cabbage, i.e., small amounts only of saturated acids and much oleic, linoleic, and linolenic acids. Especially interesting is Anderson's analysis of the acetone–ether soluble fraction of tubercle fat.[17] Palmitic, stearic, and cerotic acids were obtained from the solid fatty acid fraction. The liquid fatty acid (iodine value, 53·8) was hydrogenated, and stearic acid removed, leaving liquid unsaturated acids, which were fractionated as methyl esters in a very high vacuum. Two new acids were obtained after saponification of the two chief fractions : (1) Tuberculostearic acid, $C_{18}H_{36}O_2$, m. p. 14—15°, which is isomeric with stearic acid and shows no biological activity; (2) phthioic acid, identical with the slightly crude acid prepared from the phosphatide (see p. 207). The latter is isomeric with cerotic acid, $C_{26}H_{52}O_2$, and is optically active ($[\alpha]_D = 7\cdot98°$). The biological activity is comparable with that of the acid isolated from the phosphatide.

The very high degree of unsaturation of the glyceride fatty acids of cabbage leaves raises interesting points in connexion with the suggestion of J. B. Leathes and H. S. Raper [18] that the temperature at which fats are formed determines the degree of unsaturation. Terroine and others,[19] working with *Aspergillus niger*, and L. K. Pearson and H. S. Raper,[20] working with *A. niger* and *Rhizopus nigricans* grown at temperatures varying from 17° to 35°, have shown that the degree of unsaturation of the fatty acids falls with rise of temperature. A. C. Chibnall and H. J. Channon [14] found no significant change for winter- and summer-grown cabbage. But the very low proportion of saturated acids in the fat, together with the presence of large amounts of saturated hydrocarbon and ketone,

[15] C. G. Daubney and (Mrs.) I. S. Maclean, *Biochem. J.*, 1927, **21**, 373; *A.*, 1928, 203.

[16] J. H. Speer, E. C. Wise, and M. C. Hart, *J. Biol. Chem.*, 1928, **82**, 105; *A.*, 1928, 855.

[17] R. J. Anderson and E. Chargaff, *ibid.*, 1929, **84**, 703.

[18] "The Fats," 2nd ed., London, 1925.

[19] *Bull. Soc. Chim. Biol.*, 1927, **9**, 604.

[20] *Biochem. J.*, 1927, **21**, 875; *A.*, 1927, 906.

which can be considered as similar to them in physical properties (see p. 211), suggested that these should be included when the question of " liquidity " of the protoplasmic fats was under discussion. If this be done, the iodine value in the case of the winter-grown leaves is 137, 136 and of the summer-grown 91, 99.

These investigations of non-seed fats disclose an entirely different composition and distribution from those usually met with in seed fats, and the field promises to be a fruitful one for future research.

Aliphatic Ketones.—The presence of aliphatic methyl ketones in vegetable oils, especially essential oils, has long been known, and in 1910, H. D. Dakin [21] suggested that they are formed from the corresponding fatty acids by β-oxidation in a way analogous to his synthesis of these ketones from fatty acids by hydrogen peroxide. More detailed information concerning the production of these ketones by moulds has been obtained during the past two years. W. N. Stokoe [22] grew *Penicillium palitans* on a gelatin medium containing deodorised coconut oil, and was able to isolate methyl amyl, methyl heptyl, and methyl nonyl ketones, showing that oxidation of the corresponding fatty acids had taken place at the β-carbon atom, with the intermediary production of the β-ketonic acid. Small amounts of the corresponding secondary alcohols also were formed. The selective action of *P. palitans* and *Oidinum lactis* on fatty acids, keto-esters, methyl ketones, and carbinols was then studied. The higher fatty acids (above lauric) were not absorbed, consequently higher methyl ketones were not produced. The keto-esters were normally oxidised without the production of methyl ketones : only in the presence of fatty acids or fat, which hindered the respiration of the organism, were these substances formed. Stokoe therefore considers that the normal course of decomposition of the β-keto-acid is the formation of the fatty acid containing two carbon atoms less and acetic acid—the production of the methyl ketones is abnormal, and is due to adsorption of poisonous fatty acids in the mycelium impeding respiration. Very similar results have been obtained by O. Acklin,[23] who has studied the production of methyl ketones from fatty acids and triglycerides by *P. glaucum* : like Stokoe, he failed to obtain any evidence for the suggestion that β-hydroxy-acids are precursors of the β-keto-acids. The results, which bear out Dakin's original suggestion very completely, enable us to assume the origin of such methyl ketones as are met with in plant products.

Less clear is the metabolism of the higher aliphatic ketone and

[21] *J. Biol. Chem.*, 1908, **4**, 221; *A.*, 1908, i, 134.
[22] *Biochem. J.*, 1928, **22**, 80; *A.*, 1928, **335**.
[23] *Biochem. Z.*, 1929, **204**, 253; *A.*, 473.

corresponding paraffin isolated by H. J. Channon and A. C. Chibnall [24] from cabbage leaves. Higher paraffins, generally considered to be $C_{27}H_{56}$, $C_{29}H_{60}$, $C_{31}H_{64}$, or $C_{35}H_{72}$ from their melting points, are, in small amount, very widely distributed in the plant kingdom. The crude product isolated from the cabbage melted at 63—67° and was shown by combustion to contain about 1% of oxygen. From it, a paraffin, m. p. 62·8°, and a ketone, m. p. 80·5—81°, were obtained. S. H. Piper [25] showed by X-ray analysis that the paraffin was nonacosane, $C_{29}H_{60}$, and that the ketone also contained 29 carbon atoms. The carbonyl group was in the middle of the chain, but this was so long that he could not be certain whether the ketone was di-n-tetradecyl ketone or pentadecyl tridecyl ketone. Now the presence of a ketone so closely allied to the paraffins suggested at once the metabolism of the latter from fatty acids :

$$\begin{matrix} R_1 \cdot CO_2H \\ R_2 \cdot CO_2H \end{matrix} \longrightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!\!CO \longrightarrow \begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!\!CH_2$$
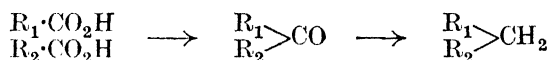
One molecule of myristic acid and one of palmitic might condense to form pentadecyl tridecyl ketone, which would yield nonacosane on reduction. Synthesis of the two ketones suggested by Piper showed, however, that the cabbage product was di-n-tetradecyl ketone, and not the unsymmetrical pentadecyl tridecyl ketone; consequently, if the above scheme of metabolism holds, the precursor of the ketone is pentadecoic acid. In view of the strong evidence now available against the occurrence in natural fats of hepta- and penta-decoic acids Channon and Chibnall prefer to leave open the question of the immediate precursor of the ketone until further experimental data are available.

Plant Sterols.—Recent advances in the chemistry of vitamin-D have rather detracted from any interest that can be gleaned from recent work on sterols in relation to the plant and plant metabolism. Recent work has, in fact, only intensified the complexity of the problem, for it has increased the number of possible phytosterols without suggesting in any way a possible mode of metabolism in the plant. Anderson and his colleagues [26] have shown that wheat germ oil, corn oil, and wheat bran fat contain no homogeneous sitosterol as had been usually found in plant products. The sterols constitute a mixture containing dihydrositosterol, and at least three isomeric forms of sitosterol, which can be separated by frac-

[24] *Biochem. J.*, 1929, **23**, 168; *A.*, 729.

[25] See previous reference.

[26] R. J. Anderson, R. L. Schriner, and G. O. Burr, *J. Amer. Chem. Soc.*, 1926, **48**, 2987; *B.*, 1927, 49; R. J. Anderson and R. L. Schriner, *ibid.*, 1926, **48**, 2976; *A.*, 1927, 49; R. J. Anderson and F. P. Nabenhauer, *ibid.*, 1926, **48**, 2997.

tionation of the acetyl derivatives and are designated α-, β-, and γ-sitosterol respectively. These differ in melting point and optical rotation. γ-Sitosterol, which is the most readily obtained by fractional crystallisation, melts at 147—148° and yields γ-sitostanol, m. p. 143—144°, on reduction. β-Sitosterol, which corresponds closely to the sitosterol of the literature, could not be obtained pure, but gave on reduction β-sitostenol, m. p. 139—140°, which corresponds closely to natural dihydrositosterol. α-Sitosterol differs from the other two isomerides in that its bromo-derivative, through which it is purified, cannot be debrominated. The presence of dihydrositosterol and γ-sitosterol in soya bean has been shown by K. Bronstedt,[27] but the latter sterol appears to be absent from rape oil. The chief sterol of yeast was shown many years ago to be identical with the ergosterol of Tanret. Mrs. I. S. Maclean [28] has since shown the presence of a second sterol, zymosterol, m. p. 108—109°, which was separated fairly readily by crystallisation. H. Wieland and M. Asano,[29] who benzoylate the yeast sterols before fractionation, claim to have isolated three further sterols. One of them gives colour reactions similar to those of ergosterol, but the other two differ from both ergosterol and zymosterol in this property.

The unsaponifiable wax obtained by R. J. Anderson [30] from tubercle bacilli (see p. 206) has not yet been completely investigated. It appears to possess both acidic and alcoholic properties.

Nitrogenous Metabolism in the Plant.

Methods of Analysis of Nitrogenous Products in Plant Material.— In recent methods for estimating the various forms of nitrogen in plant extracts there is evidence of a more critical outlook which is very welcome. The Van Slyke method for estimating amino-nitrogen, introduced in 1912 and followed by his now well-known method of determining nitrogen distribution in proteins, naturally appealed to plant chemists and was applied somewhat indiscriminately to plant extracts. It was tacitly assumed that these extracts would have a composition similar to that of a protein digest—an assumption which seemed well founded in light of the older work of E. Schulze and his school at Zürich. Most of this work, however, was fragmentary and a complete investigation of the aqueous extract of lucerne enabled H. B. Vickery [31] to show quite definitely that its composition was more complex than had hitherto been supposed. The " basic " nitrogen precipitated by phosphotungstic acid was a

[27] *Z. physiol. Chem.*, 1928, **176**, 269.
[28] *Biochem. J.*, 1928, **22**, 22; *A.*, 1928, 329.
[29] *Annalen*, 1929, **473**, 300; *A.*, 1200.   [30] *J. Biol. Chem.*, 1929, **85**, 339.
[31] *Plant Physiol.*, 1927, **2**, 303; *A.*, 1928, 107.

very complex mixture containing only small amounts of the hexone bases. Many non-basic nitrogenous substances, as well as peptides yielding large amounts of monoamino-acids on hydrolysis, were present. Vickery therefore considers that the determination of " basic " nitrogen in plant extracts may be very misleading, and does not recommend it. His summary of the lucerne investigation, which has unfortunately been published in a report [32] difficult of access to European investigators, should be read by all interested in plant nitrogen. Only 22% of the soluble nitrogen was accounted for in crystalline form; yet the Van Slyke method is assumed to account for 3—4 times this amount in most plant extracts. Modifications of this method are also required if the extract or plant material contains volatile bases such as nicotine, cyanogenetic glucosides, or much nitrate. H. B. Vickery and G. W. Pucher [33] determine the preformed ammonia and " amide " nitrogen in tobacco extracts by the method of O. Folin and L. E. Wright,[34] using permutite to separate the ammonia from free nicotine in the distillate. Foreman's method,[35] referred to in last year's Report, should be applicable here. For the determination of nicotine itself, attention may be directed to papers by J. Bodnár and V. L. Nagy [36] and by F. D. Chattaway and G. D. Parkes.[37]

The latter workers make use of the fact that the base forms a crystalline, stable, and sparingly soluble tetrachloroiodide. By means of it nicotine can be easily and accurately estimated, since in the presence of a large excess of hydrogen chloride it separates practically quantitatively, even from dilute solutions, as a heavy precipitate which can be collected on a Gooch crucible and dried without loss. Alternatively, the precipitate collected on the crucible may be added to an excess of a warm concentrated solution of potassium iodide acidified with acetic acid, and the iodine liberated estimated by sodium thiosulphate. H. B. Vickery and G. W. Pucher [38] have determined the apparent dissociation constants of nicotine, and make use of these to determine the proportion of free (volatile) nicotine and nicotine present as salts in tobacco, which is of industrial importance.

That the usual method of determining nitrate nitrogen by Devarda's alloy may give misleading results in the presence of certain plant constituents, such as asparagine, was first pointed out by

[32] Quoted in T. B. Osborne and L. B. Mendel, " Year Book," *Carnegie Institution of Washington*," 1925, **24**, 354.

[33] *J. Biol. Chem.*, 1929, **83**, 3.

[34] *Ibid.*, 1919, **38**, 461; *A.*, 1919, ii, 371.

[35] *Ann. Reports*, 1928, **25**, 235.

[36] *Biochem. Z.*, 1929, **206**, 410; *A.*, 729.

[37] *J.*, 1929, 1314, 2817; *A.*, 729.   [38] *J. Biol. Chem.*, 1929, **84**, 233.

R. C. Burrell and T. G. Phillips,[39] who recommended a modification of the phenoldisulphonic acid method.   The errors due to the presence of cyanamide or urea (in the case of fertilisers) were overcome by C. H. Jones, who carried out the reduction of the nitrate in acid solution by means of reduced iron powder.[40]   This method has recently been modified and applied to plant extracts by H. B. Vickery and G. W. Pucher [41] so as to permit the determination of nitrate nitrogen in the presence of volatile bases such as nicotine.   Other papers dealing with the determination of nitrate nitrogen in plant tissues should be noted.[42]

The presence of cyanide nitrogen in plants, due either to free hydrocyanic acid or to cyanogenetic glucosides, is generally ignored by workers in this field.   That the glucosidic cyanogen was very labile was pointed out by M. Traube [43] and later workers; a loss, for instance, of as much as 6% of the hydrogen cyanide may be incurred by plunging the leaves into boiling alcohol.   L. R. Bishop [44] has recently devised a method whereby most of the cyanogenetic glucoside is decomposed by heating with water, and the remainder by emulsin.   The operation is performed in a closed apparatus through which air is drawn, and the liberated hydrogen cyanide is estimated by absorption with potash.   Methods of determining the nitrogen partition in cyanophoric plants, based on the above, have been worked out by Miss M. E. Robinson [45] and applied to *Prunus laurocerasus*.   A committee of the American Society of Plant Physiology have issued recommended methods for the chemical analysis of plant tissues, dealing with such factors as sampling, drying of tissues and the determination therein of carbohydrates, fats and various forms of nitrogen, etc.[46]   These recommendations are based on the personal experience of workers in the respective fields, and should prove a useful guide to those whose training and interest are in the biological side of plant problems.

In 1927, R. Fosse [47] announced the identification of a new nitrogenous substance, allantoic acid, in *Phaseolus vulgaris*, which is precipitated from the expressed juice as dixanthylallantoic acid

[39] *J. Biol. Chem.*, 1925, **65**, 229; *A.*, 1925, i, 1367.
[40] *Ind. Eng. Chem.*, 1927, **19**, 267; *B.*, 1927, 262.
[41] *Ibid.*, Analytical Ed., 1929, **1**, 121.
[42] E. M. Emmert, *Science*, 1928, **68**, 457; *A.*, 1928, 762; Sessions and Shive, *Plant Physiol.*, 1928, **3**, 499; H. F. Holtz and C. Larson, *ibid.*, 1929, **4**, 285.
[43] *Ann. Jard. Bot. Buitenzorg.*, 1907, **21**, 101.
[44] *Biochem. J.*, 1927, **21**, 1162; *A.*, 1927, 1228.
[45] *Ibid.*, 1929, **23**, 1099; *A.*, 1345.
[46] *Plant Physiol.*, 1926, **1**, 397; 1927, **2**, 195, 205, 497.
[47] *Comp. rend.*, 1926, **183**, 1114; *A.*, 1927, 284.

by means of xanthhydrol and purified through the mercury salt.[48] It can be determined quantitatively by acid hydrolysis to urea, which is then estimated as xanthylurea in the usual way with xanthhydrol. Applied to the extract from *Acer pseudoplatanus*, the method gave yields of allantoic acid as high as 0·68 g. per kilo. of fresh leaf material. Investigation of several seeds, especially *Soya hispanida*, shows that they contain an enzyme, allantoinase, which will hydrolyse allantoin to allantoic acid.[49] Making use of the fact that the seed also contains urease, Fosse [50] has devised a method for determining allantoin in the presence of urea. He states, further,[51] that some seeds contain a third enzyme, an oxidase, capable of transforming uric acid into allantoin. A modified method of determining urea as dixanthyl urea has been devised by F. W. Allen and J. M. Luck.[52]

Methods of estimating the relative amounts of various proteins in seeds, so that changes during ripening and germination may be followed, have received but little attention. P. F. Sharp and B. L. Herrington [53] have investigated the proteins of wheat, and L. R. Bishop [54] those of barley, from this point of view.

The Transport of Nitrogenous Substances in Plants.

In last year's Report the contributions of T. G. Mason and E. J. Maskell [55] to the problem of the transport of carbohydrates were briefly mentioned. This year there falls to be recorded a continuation of their researches on the cotton plant, in which the variations in gross amount and the flow of nitrogen between the leaves and bark have been investigated. Their results on the diurnal variations in leaf nitrogen come at an opportune time, as certain of the earlier results recorded in the literature [56] have recently been called into question. A. C. Chibnall [57] concluded from a review of previous work, and from his own experiments with *Phaseolus multiflorus*, that if the quantity of nitrogen in the leaf was expressed in terms of the fresh weight of the leaf there was undoubtedly a fall in total nitrogen in the leaf during the night, which was shown to be due to the decomposition of protein and the translocation of the resulting

[48] R. Fosse and A. Hieulle, *Bull. Soc. Chim. Biol.*, 1928, **10**, 310; *A.*, 1928, 803.
[49] R. Fosse and A. Brunel, *Comp. rend.*, 1929, **188**, 426; *A.*, 353.
[50] R. Fosse, A. Brunel, and P. de Graeve, *ibid.*, p. 1418; *A.*, 847.
[51] *Ibid.*, 1929, **189**, 213; *A.*, 1107.
[52] *J. Biol. Chem.*, 1929, **82**, 693; *A.*, 962.
[53] *Cereal Chemistry*, 1927, **4**, 249; *B.*, 1927, 761.
[54] *J. Inst. Brewing*, 1928, **34**, 101; 1929, **35**, 316.
[55] *Ann. Reports*, 1928, **25**, 229.
[56] Reviewed by Miss M. E. Robinson, *New Phyt.*, 1929, **28**, 117.
[57] *Ann. Reports*, 1923, **20**, 223; 1924, **21**, 192.

products probably in the form of asparagine.   Miss C. A. Gouwentak [58] has queried the validity of these results, on the ground that the percentage fall in total nitrogen observed ($2 \cdot 5 \pm 0 \cdot 2$) was small, and that the fresh-weight basis for nitrogen comparison is not physiologically sound.   She cites experiments of her own on *Helianthus annuus*, showing no significant variation during the night when the leaf nitrogen is expressed as mg./dm.^{2} of leaf surface.   P. K. Mottes,[59] who worked with *Vicia faba*, *Lupinus lutens*, and *Phaseolus multiflorus*, obtained results of the same order as Chibnall's : there was a fall in total nitrogen and protein nitrogen during the night on both a fresh-weight and a leaf-area basis of comparison. As the three main variables in the leaf—water, carbohydrates, and nitrogenous products—can all vary independently, it will be realised that any basis of comparison must rest on assumptions the validity of which may be doubtful, or at any rate, open to discussion. As the carbohydrate fluctuation is the greatest, E. J. Maskell and T. G. Mason [60] express their results on the basis of residual dry weight (dry weight less total carbohydrates) as well as on the basis of fresh weight.

The earlier workers mentioned above made their diurnal comparison between samples collected in the evening and on the following morning.   With far more experimental material available, Maskell and Mason have been able to make collections at intervals of 3 hours over a period of 36 hours.   Each collection consisted of two samples, each of which consisted of three mature leaves taken from each of twenty plants.   By both their methods of comparison there was a fall, allowing for sampling error, of about 4% in total nitrogen during the night.   That this can be ascribed to the transport of organic nitrogenous substances synthesised in the leaf follows from further observations.   By regional analysis of the plant tissue the authors show that there is a gradient of organic non-protein nitrogen outwards from the leaf, *i.e.*, the concentration is greatest in the leaf parenchyma and shows a progressive fall on passage, *via* the main veins and petiole, downward through the bark.   Further, the gradient in nitrate nitrogen—which ringing experiments show is translocated upwards through the wood, and not through the bark as suggested by O. F. Curtis [60a]—is in the opposite direction. That protein synthesis from nitrate therefore takes place in the leaves, and that these organs supply nitrogen in organic form to other parts of the plant during the night would seem now to be

[58] *Rec. trav. bot. néerlandais*, 1929, **26**, 19.
[59] *Z. wiss. Biol.*, Abt. E., 1926, **1**, 472.
[60] *Ann. Bot.*, 1929, **34**, 205, 615; *A.*, 854.
[60a] *Amer. J. Bot.*, 1923, **10**, 361.

fairly well established. The gradient of organic non-protein nitrogen, as mentioned above, is downwards from the leaf to the bark, and analysis shows that this is due mainly to what the authors refer to as the residual nitrogen and to amino-nitrogen. The asparagine nitrogen shows a progressively higher concentration on passage from the leaf parenchyma down to the sieve tubes, and laterally from the sieve tubes to the rays. Maskell and Mason therefore suggest that the residual and the amino-nitrogen may be concerned mainly with transport and that asparagine is connected mainly with storage. This conclusion is interesting in that it supports the general hypothesis of Prianischnikoff, who opposes the view, originally propounded by Pfeffer and supported by Schulze and Chibnall, that asparagine, besides serving as a storage of ammonia, is also one of the substances in which organic nitrogen in a form suitable for easy resynthesis of protein is conveyed from one part of the plant to another.[61]

The interpretation of all their experimental data by Maskell and Mason on a gradient basis is naturally open to argument, but there can be no doubt as to the interest of their results, and as to the advance that they have made in methods of experimentation. It would seem that the problem of translocation of nitrogen in the plant will be solved only when the sieve-tube sap can be collected in quantity sufficient for chemical analysis, and this, unfortunately, presents experimental difficulties that cannot be overcome at the present time. The above-mentioned workers discuss briefly the factors responsible for the movement of organic nitrogen in the sieve tubes and find that the problem is here even more complex. The effect of constricting the channel of transport (by partial ringing of the bark) suggests that diffusion is a factor in the process of transport, but that the rate of movement is greatly in excess of that due to diffusion alone. It appears probable that, as in the case of sugar transport, there is some agency at work accelerating diffusion in the sieve tubes.

The Development of Proteins in the Seed.—The form in which nitrogen is translocated in the plant again becomes a crucial question when some recent work on the synthesis of protein in the ripening seed is considered. E. Schulze [62] showed that the husks of several leguminaceæ contain considerable quantities of asparagine, with small amounts of the usual protein amino-acids, choline, trigonelline, etc. The developing embryo, unlike the husk, contains little or no asparagine, and consequently Schulze assumed that the asparagine translocated from the leaves passed first of all into the husk and

[61] See footnote, ref. 56.
[62] *Z. physiol. Chem.*, 1911, **71**, 31; *A.*, 1911, ii, 322.

thence into the embryo. A. Kiesel [63] has carried out similar experiments with ripening rye ears, and has noted, together with the other substances mentioned above, the presence of relatively large amounts of aspartic acid and the complete absence of asparagine. This observation led him to discuss as one alternative the possibility that amino-acids, etc. (Bausteine), were translocated to the active centres of the developing grain in excess of requirements, and that the excess was stored as aspartic acid instead of the more usual asparagine. The evidence for this point of view, however, is not very convincing. All investigators seem to agree that no accumulation of simple nitrogenous products occurs at any stage during the ripening of the grain, showing that as fast as these substances enter the immature grain they are used for the synthesis of protein. It is to be expected, then, that under these conditions of intense synthetic activity asparagine would undergo almost immediate deamidation (for enzymes capable of doing this are known to occur in the plant) [64] to provide ammonia for amino-acid and protein synthesis. The presence of much aspartic acid in the ripening rye ears, therefore, is not incompatible with the theory of the translocation of asparagine from the leaves to the active centres in the developing grain, as Kiesel admitted as a second alternative.

With regard to the development of the individual proteins in the grain, H. E. Woodman and F. L. Engledow [65] have shown that in wheat the two main proteins, gliadin and glutenin, appear in the quite immature grain (33 days from ear emergence), and that the increase in the amount of gliadin is more rapid than that of glutenin. At the end of 50 days the first signs of coherent gluten formation were observed, denoting a critical stage in the development of the grain marking the beginning of the desiccation period. Thereafter the amount of glutenin remained roughly constant, but the gliadin content continued to increase until complete maturity of the grain.

L. R. Bishop,[66] using somewhat more elaborate methods of analysis, has traced the development of the proteins in the barley grain. Sampling was commenced at a correspondingly earlier period than that observed by Woodman and Engledow (6 days after anther emergence), and it was found that albumin and globulin were the chief proteins then being formed. The quantity of glutelin was at first greater than that of hordein, but the rate of synthesis of the latter was more rapid and in the final stages the amount of it

[63] *Z. physiol. Chem.*, 1924, **135**, 61; *A.*, 1924, i, 689; see also *Ann. Reports,* 1925, **22**, 212.

[64] See footnote, ref. 56.

[65] *J. Agric. Res.*, 1924, **14**, 563; *A.*, 1925, i, 217.

[66] Ph.D. Thesis, Cambridge, not yet published.

exceeded that of the glutelin. The developmental curves obtained by Bishop show that there is a regular relationship between the amounts of the individual proteins and the total nitrogen of the individual grain, suggesting that the nitrogen entering the grain is partitioned out regularly to the various centres synthesising the proteins on some mass-action or related basis. In other words, the relative amounts of hordein and glutelin in the mature grain are determined solely by the total nitrogen of the grain, and are unaffected by conditions such as soil or season except in so far as these affect the supply of nitrogen to the plant. This relationship appears to hold within a variety or strain, as has been shown by many analyses of mature grains of Plumage Archer of total nitrogen varying between 1·2% and 2·4% of the dry weight. Differences in protein distribution occur between varieties.

Seed Proteins.

The application of existing methods is slowly adding to our knowledge of the proteins of seeds. The chief interest perhaps is to be found in the extension of work on cereal proteins. W. F. Hoffman and R. A. Gortner [67] have prepared several new alcohol-soluble proteins of the gliadin class, all of which have been analysed by the Van Slyke method.

D. B. Jones [68] and his co-workers have investigated many new glutelins, which they prepare by extracting the cereal meal with 60% alcoholic potash and acidifying the extract to throw down the crude glutelin—the gliadin remaining in solution. The glutelin is purified by re-solution in alkali and reprecipitation. On treatment of an aqueous sodium hydroxide solution with ammonium sulphate, an α-glutelin separates at about 3% saturation and a β-glutelin at about 16% saturation.

These methods of preparing glutelins have been called into question by M. J. Blish and R. M. Sandstedt.[69] Reviewing the published data for the amide- and the arginine-nitrogen for wheat glutenin, they find variations from 12·4% to 18·8% and from 8·18% to 12·94%, respectively. They first showed that both these values varied with the strength of the alkali used during the initial extraction, and have in consequence evolved a method whereby the glutenin can be prepared without coming into contact with alkali

[67] Colloid Symposium Monograph, 1925, **2**, 209.

[68] F. A. Csonka and D. B. Jones, *J. Biol. Chem.*, 1927, **73**, 321; *A.*, 1927, 799; D. B. Jones and F. A. Csonka, *ibid.*, 1927, **74**, 427; *A.*, 1927, 1227; F. A. Csonka and D. B. Jones, *ibid.*, 1927, **75**, 189; *A.*, 1927, 1227; D. B. Jones, *ibid.*, 1928, **78**, 289; *A.*, 1928, 1063; F. A. Csonka and D. B. Jones, *ibid.*, 1929, **82**, 17; *A.*, 857.

[69] *Ibid.*, 1929, **85**, 195.

at all.   Acetic acid diluted with methyl alcohol to an alcoholic
concentration of 70% is used as solvent.   Starch, etc., are removed
by centrifuging, and the glutenin is precipitated at p_H 7·0 without
excess of alkali being present at any time.   The treatment is re-
peated many times and the glutenin is finally extracted with 70%
alcohol to remove traces of gliadin.   Thus prepared, it has physical
properties quite distinct from those of ordinary glutenin and contains
22% of amide-nitrogen and only 9% of arginine-nitrogen.   Treat-
ment with aqueous alkali in the way customary for the preparation
of glutelins leads to products similar to those obtained by previous
workers.   Part of the nitrogen, however, remains in solution, and
on hydrolysis this material gives 25% of amide-nitrogen and 7—8%
of arginine-nitrogen—values similar to those given by gliadin.   Blish
and Sandstedt consider that these results show clearly that true
" glutenin " is more complex than either gliadin or what has
generally been regarded as glutenin, that it undergoes an irreversible
alteration in chemical structure when dispersed in an alkaline
medium, and that this factor has influenced the composition and
properties of all the so-called glutelins that have been so far prepared
from other cereals.

Synthesis of Phytol.

F. G. Fischer and K. Löwenberg have now brought to a successful
conclusion their research into the constitution of phytol, the alcohol
component of chlorophyll.   R. Willstätter and his co-workers in
1911 [70] obtained by oxidation of phytol a ketone which they con-
sidered to be $C_{17}H_{34}O$.   Fischer and Löwenberg [71] reduced the
ozonide of phytol—a C_{20} compound—with hydrogen in presence of
palladised calcium carbonate and obtained glycollaldehyde and this
same ketone, which must therefore be $C_{18}H_{36}O$.   They next assumed
that phytol was built up of reduced isoprene units, and that its
constitution might be 3 : 7 : 11 : 15-tetramethyl-Δ^2-hexadecen-1-ol
(IV).   This would give on hydrolysis of the ozonide a ketone,
6 : 10 : 14-trimethylpentadecan-2-one   (I).   The latter substance
was accordingly synthesised from farnesol, and was found to be
identical with the ketone derived from phytol.   The constitution of
phytol thus established has now been confirmed by synthesis.[72]
The ketone (I) was synthesised this time from ψ-ionone,[73] and on
condensation with acetylene it yielded 3 : 7 : 11 : 15-tetramethyl-
Δ^1-hexadecinen-3-ol (II).   On reduction with hydrogen and

[70] Annalen, 1910, **378**, 73; 1919, **418**, 121; A., 1911, i, 144; 1919, i, 448.
[71] Ibid., 1928, **464**, 69; A., 1928, 989.
[72] Ibid., 1929, **475**, 183; A., 1421.
[73] I. M. Heilbron and A. Thompson, J., 1929, 883; A., 790, had meanwhile
reported the synthesis of the ketone from farnesol.

palladised calcium carbonate, this gave $3 : 7 : 11 : 15$-tetramethyl-Δ^1-hexadecen-3-ol (III). Warmed with acetic anhydride for some hours at $100°$, (III) gave the acetate, which underwent anionotropic change with the formation, together with other products, of $3 : 7 : 11 : 15$-tetramethyl-Δ^2-hexadecen-1-ol (IV), identical in all respects with natural phytol.

(I.) $CHMe_2 \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot COMe$

$$\downarrow CH\dot{\cdot}CH$$

(II.) $CHMe_2 \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot CMe(OH) \cdot C\dot{\cdot}CH$

$$\downarrow H_2$$

(III.) $CHMe_2 \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot CMe(OH) \cdot CH\dot{\cdot}CH_2$

(IV.) $CHMe_2 \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot CHMe \cdot [CH_2]_3 \cdot CMe\dot{\cdot}CH \cdot CH_2 \cdot OH$
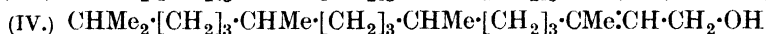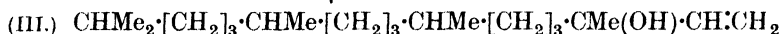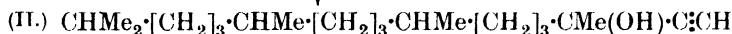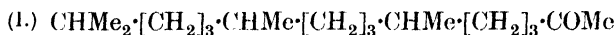
Glutathione.

Interesting developments in the chemistry of glutathione have taken place during the course of the year. (Sir) F. G. Hopkins,[74] who first isolated this substance in 1921, produced evidence, which at the time seemed quite satisfactory, that it was a dipeptide, diglutamylcystine. The analytical data for sulphur and total nitrogen were in fair agreement with this structure, though the amino-nitrogen, as determined by Van Slyke's method, was somewhat high. Hopkins's structure seemed to be confirmed by the synthesis of diglutamylcystine by C. P. Stewart and H. E. Tunnicliffe.[75] The first suggestion that the dipeptide structure was not in complete accordance with analytical data came from G. Hunter and B. A. Eagles,[76] who obtained fairly clear evidence that the material hitherto called glutathione, and considered a chemical entity, contained another amino-acid. Hopkins at first doubted this new evidence,[77] but a long reinvestigation in his laboratory, undertaken to confirm or refute it, has shown definitely that a third amino-acid, glycine, is undoubtedly present in all preparations of glutathione.[78] The new evidence shows that the substance is a tripeptide, and it has now been obtained in crystalline form not only by Hopkins, but also by E. C. Kendall and his co-workers, whose researches are discussed a little later. Hopkins has revised his technique for the preparation of glutathione, and now obtains a yield of the order of 1 g. per kilo. of fresh yeast by precipitating the tripeptide as a cuprous salt in the presence of $0.5N$-sulphuric

[74] Biochem. J., 1921, 15, 286; A., 1921, 635.
[75] Ibid., 1925, 19, 207; A., 1925, i, 795.
[76] J. Biol. Chem., 1927, 72, 147; A., 1927, 477.
[77] Ibid., p. 185; A., 1927, 478.
[78] Ibid., 1929, 84, 1269; A., 1491; Nature, 1929, 124, 445; A., 1322.

acid. It is undoubtedly a tripeptide of glutamic acid, glycine and cysteine, but the analysis for amino-nitrogen by Van Slyke's method gives a value nearly 50% in excess of that which would be given by a single free amino-group, an observation which, as Hopkins points out, helps to explain his bias towards the dipeptide structure assigned to the original crude glutathione. That the Van Slyke figure is actually in excess of the true free amino-nitrogen would appear to follow from the observation of L. J. Harris reported in Hopkins's paper, and from the electrometric titrations of N. W. Pirie and K. G. Pinhey made in his laboratory.[79] Hopkins is not yet prepared to assign a definite structure to the tripeptide, but records many observations which show that under certain conditions the molecule displays a degree of instability which is unusual, even when compared with the somewhat unstable cystine-containing peptides synthesised by M. Bergmann.[80] It is impossible here to recount them in full, but briefly stated they are : (1) sulphur is readily removed by alkali in the presence of lead acetate, (2) aeration at room temperature at p_H 7·6 brings about the conversion of only 80% of the thiol into the disulphide form, the remainder of the substance losing both sulphur and nitrogen, (3) when the tripeptide is boiled in pure aqueous solution, much decomposition occurs, and, together with other unidentified products, the diketopiperazine of glycine and cysteine (or, in the case of the disulphide form, diglycylcystine dianhydride) and glutamic acid have been isolated. Decomposition extends to the carbon atoms, and nearly 14% of the carbon is lost as carbon dioxide after 50 hours' boiling.

Almost simultaneously with the publication of Hopkins's new results appeared those of E. C. Kendall [81] and his associates. The original method of isolating glutathione has been improved and the compound obtained crystalline. Analysis of the product again leaves no doubt that it is a tripeptide of glutamic acid, cysteine and glycine, to which they give the tentative formula

$HO_2C\cdot CH_2\cdot NH\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot SH$

on the following evidence : (1) After treatment with nitrous acid and long hydrolysis with concentrated hydrochloric acid, they were able to isolate glycine as hippuric acid, but no glutamic acid. This shows that the glycine is attached through its amino-group, and that the amino-group of the glutamic acid is not substituted. (2) The action of hydrogen peroxide in the presence of ammonia gives

[79] *J. Biol. Chem.*, 1929, **84,** 321; *A.,* 1492.

[80] M. Bergmann and F. Stather, *Z. physiol. Chem.,* 1926, **152,** 189; *A.,* 1926, 631.

[81] E. C. Kendall, B. F. McKenzie, and H. L. Mason, *J. Biol. Chem.,* 1929, **84, 656.**

carbon dioxide, and after hydrolysis no glycine or glutamic acid could be separated, but only succinic acid. This shows that probably the amino-group of the glycine is attached to the α-carboxyl group of the glutamic acid.

It does not appear to the Reporter that the last conclusion is valid.[82a] Moreover, the formula proposed is in direct conflict with some of Hopkins's results : it does not explain, for instance, the formation of the diketopiperazine of glycine and cysteine on boiling in aqueous solution. Further results will be awaited with great interest. In the meanwhile, M. Dixou and N. U. Meldrum [82] have stated that the tripeptide is physiologically inert; the undoubted activity of the older impure glutathione preparations in this respect, therefore, still remains an unsolved mystery.

Cerebrosides.

During the past few years E. Klenk has published a series of papers on brain cerebrosides, and some of his recent conclusions have an interesting bearing on the structure of sphingosine and cerebronic acid.

Sphingosine has been considered to be a dehydroheptadecylamine, $CH_3\cdot[CH_2]_{11}\cdot CH\dot:CH\cdot C_3H_4(OH)_2\cdot NH_2$, chiefly from the work of P. A. Levene and C. J. West. On oxidation with chromic acid they [83] obtained an acid, m. p. 48—49°, which was considered to be pure n-tridecoic acid, because its mixed m. p. with a sample of synthetic acid was unchanged and its amide melted at 98—99°. Oxidation of dihydrosphingosine gave an acid (mol. wt. 250) melting at 53°, which they considered to be n-pentadecoic acid (mol. wt. 242). In an earlier paper,[84] products melting at 60—61° (mol. wt. 243) were described. At that time Levene [85] accepted 51° as the m. p. of his purest synthetic tridecoic acid, although he withdrew it the following year [86] and substituted 45·5°, which is still 2° higher than the m. p. recorded by any other observer. E. Klenk [87] has repeated this work, and finds that the acid obtained by oxidation of sphingosine melts after intensive purification at 52·5—53° and gives analytical figures for myristic acid. The acid obtained by oxidation of dihydrosphingosine melts at 62° and is shown to be

[82] *Nature*, 1929, **124**, 512; *A.*, 1334.

[82a]. A paper by Kendall and his associates (*Proc. Mayo Clinic*, 1929, **4**, 359) appeared after this Report had been sent to the printer. New evidence shows that the formula in the text is untenable, and that the tripeptide is probably γ-glutamylcysteinylglycine. This was thought to be the most probable formula by Pirie and Pinhey, and is not in conflict with Hopkins's results.

[83] *J. Biol. Chem.*, 1914, **18**, 482.　　　　[84] *Ibid.*, 1913–4, **16**, 553.

[85] *Ibid.*, 1914, **18**, 467.　　　　[86] P. A. Levene *et al.*, *ibid.*, 1915, **23**, 71.

[87] *Z. physiol. Chem.*, 1929, **185**, 169.

palmitic acid. Klenk therefore considers that sphingosine contains 18 carbon atoms and is $CH_3\cdot[CH_2]_{12}\cdot CH\!:\!CH\cdot C_3H_4(OH)_2\cdot NH_2$. His analytical data seem convincing, and there would appear to be but little doubt that Levene was misled by the high m. p. of his initial synthetic tridecoic acid. Klenk [88] has also attacked Levene's structure for cerebronic acid (α-hydroxypentacosoic acid of the lignoceric acid series), alleging that on oxidation with permanganate it gave a tricosoic acid and not lignoceric acid. Levene and F. A. Taylor [89] repeated their previous work and refused to accept this conclusion. Klenk [90] then treated cerebronic acid with hydriodic acid and obtained lignoceric acid : accordingly he re-stated his view that cerebronic acid was α-hydroxylignoceric acid. Taylor and Levene [91] have now given a more lengthy reply. In the first place they emphasise the fact that in their original paper of 1922 [92] they pointed out the possibility of the occurrence of other acids in addition to cerebronic in the fraction composed principally of that acid. They have oxidised a large quantity of cerebronic acid and have fractionated the esters of the resulting crude acids. A fraction yielding a tetracosoic acid, mol. wt. 367, m. p. 78·5—79·5°, similar to the one previously prepared, was readily obtained. From the lower-boiling esters, an acid of mol. wt. 356 and m. p. 77·8—78·6°, corresponding to Klenk's tricosoic acid, was also obtained, but on further fractionation it was shown to be impure—together with acids of higher molecular weight, it yielded an acid which gave the analytical figures of docosoic acid (m. p. 74·2—75·2°), but which was shown on more exhaustive fractionation to contain material of still lower molecular weight. Taylor and Levene are convinced that the present results show that the cerebronic acid fraction was originally a mixture of acids, some of which may not belong to the lignoceric series, and therefore that the question of the number of cerebrosides occurring in tissues, as well as the problem of the structure of the fatty acids entering into their structure, is in need of re-investigation.

Crystalline Insulin.

During the past year the elucidation of the problem of the homogeneity or otherwise of the crystalline insulin first isolated from the commercial product by Abel has been materially furthered.[93]

[88] *Z. physiol. Chem.*, 1928, **174**, 214; *A.*, 1928, 868.

[89] *J. Biol. Chem.*, 1928, **80**, 227; *A.*, 321.

[90] *Z. physiol. Chem.*, 1928, **179**, 312; *A.*, 321.

[91] *J. Biol. Chem.*, 1929, **84**, 23; *A.*, 1479.

[92] *Ibid.*, 1922, **52**, 227; *A.*, 1922, i, 714.

[93] *Ann. Reports*, 1926, **23**, 238; 1927, **24**, 261; 1928, **25**, 261.

One of the most important contributions in this field is that of C. R. Harington and D. A. Scott.[94] These workers have obtained from the crude material, by the use of a simpler modification of Abel's method and also by a method of their own, active crystalline preparations of which the uniform activity indicates " that their substance has a closer relation to the specific insulin activity than that of an inert adsorbent of an intensely active contaminant." In Harington and Scott's own method of inducing crystallisation the solution of insulin is treated with saponin and ammonia, centri- fuged, and adjusted to p_H 5·6, and from this solution the micro- crystalline product separates on keeping in rhombohedra approxim- ating to cubes which are standing on one corner and thus appear under the microscope in hexagonal outline. They are weakly doubly refracting with a refractive index of approximately 1·58. Digitonin may be used in place of saponin.

Batches of the crystalline material prepared by different methods were assayed by four independent workers (K. Culhane, H. P. Marks, D. A. Scott, and J. W. Trevan [95]), the average result being 23·3 international insulin units per mg., with a standard deviation from the mean of $\pm$ 0·6. K. Freudenberg and W. Dirscherl [96] record the value of 26 international units per mg. for a preparation of crystalline insulin obtained from Professor Abel. H. Jensen, O. Wintersteiner, and E. M. K. Geiling [97] have prepared crystalline insulin from the islet tissue of the cod and pollock and find that it is identical in crystalline form, physiological activity, and in its sulphur and nitrogen contents with that prepared from bovine insulin. These workers find that the activity of both fish and bovine insulin is about 24 international units per mg., which is in close accord with the figure obtained by Harington and Scott. The latter workers [98] point out that there exist amorphous prepar- ations available commercially with an activity in the neighbourhood of 20, and sometimes as high as 22, units per mg., and infer that the production of crystals from such material would accordingly not entail the preparation of a highly active principle from a crude mixture, but rather the creation of conditions allowing the crystal- lisation of a substance already almost pure. The analogy is therefore with the crystallisation of serum-albumin rather than with the isolation of a hormone such as adrenaline, a conclusion which is supported by the observations of K. Freudenberg, W. Dirscherl, and H. Eyer,[99] who find that by the Debye–Scherer method the

[94] *Biochem. J.*, 1929, **23**, 384; *A.*, 851.   [95] *Ibid.*, p. 397; *A.*, 851.
[96] *Z. physiol. Chem.*, 1929, **180**, 212; *A.*, 357.
[97] *J. Pharm. Exp. Ther.*, 1929, **36**, 115; *A.*, 851.   [98] *Loc. cit.*
[99] *Naturwiss.*, 1929, **17**, 603; *A.*, 1110.

crystals do not behave differently from amorphous insulin and therefore resemble protein crystals. Crystalline insulin is therefore regarded as being the true active principle of the gland in so far as the function of the latter in relation to carbohydrate metabolism is concerned. It is suggested that, as in the case of iodothyreoglobulin, the physiological activity is a property, not of the protein as a whole, but of a specific constituent or grouping contained within its molecule. The comparison of the thyroid protein and insulin is of great interest, and Harington and Scott conclude their remarks as follows :

" The thyroid protein is differentiated from other proteins in an obvious manner by its iodine content, and the specific constituent, being a simple amino-acid, can be readily separated from the rest of the molecule ; the insulin protein bears no such chemical earmark, unless it be the high content of sulphur. The analogy which we have drawn between the thyroid protein and the insulin protein must not be taken to indicate that we believe such a separation of the specific group to be necessarily practicable in the latter case. As a theoretical possibility, however, it seems worth bearing in mind."

Moreover it suggests a possible explanation for some remarkably high unitage values already recorded in the literature.[1]

W. Dirscherl[2] has published interesting observations on the action of pepsin on insulin, on acetyl insulin, and on the material regenerated from acetyl insulin.[3] He finds that the inactivation of insulin by pepsin is comparable with the digestion of a protein by that enzyme, the process having an optimum of p_H 1·8 at 45°. Acetyl insulin is only slightly affected after three hours of such treatment. In accord with these results it is found that formol titration of a pepsin-insulin digest shows an increase in amino-nitrogen (from 10 to 18% of the total nitrogen), whilst acetyl insulin shows only a slight increase after 24 hours. F. Bischoff and M. Sahyun[4] have studied the denaturation of insulin by concentrated ice-cold sulphuric acid, and find that the product, which is acid-insoluble at p_H more acid than 4·8, retains half its potency : addition of formaldehyde to the sulphuric acid completely destroys the potency of the final product. The denaturation by sulphuric acid is irreversible. Further data on this subject have been recorded by K. Freudenberg, W. Dirscherl, and H. Eyer,[5] who find

[1] H. Jensen and E. M. K. Geiling, *Ann. Reports*, 1928, **25**, 262; V. du Vigneaud, E. M. K. Geiling, and C. A. Eddy, *J. Pharm. Exp. Ther.*, 1928, **33**, 497; *A.*, 1928, 1160; F. Bischoff and M. Sahyun, *J. Biol. Chem.*, 1929, **81**, 167; *A.*, 358.

[2] *Z. physiol. Chem.*, 1929, **180**, 217; *A.*, 357.

[3] *Ann. Reports*, 1928, **25**, 262.

[4] *J. Biol. Chem.*, 1929, **81**, 167; *A.*, 358.   [5] *Loc. cit.*

that the slow inactivation of insulin by means of formaldehyde is partly reversible under the action of very dilute hydrochloric acid, and suggest that the inactivation is not due to the action of formaldehyde on amino-groups. B. Stuber and K. Lang [6] state that in weakly alkaline solutions condensation compounds of insulin and cholic or deoxycholic acid are formed. Cholylinsulin and deoxycholylinsulin are physiologically active when administered either subcutaneously or orally. The two methods of administration are stated to be equally effective, but the dose must be large, some 200—300 units.

The Chemistry of Muscle Processes.

Adenylic Acid and the Formation of Ammonia in Muscle.—In the Report of last year [7] reference was made to a series of papers from Embden's laboratory dealing with the subject of the functional formation of ammonia in muscle and the relationship of adenylic acid to this process. In the first of these communications G. Embden, C. Riebeling, and G. E. Salter [8] give results which demonstrate that the formation of ammonia in freshly minced frog- and rabbit-muscle pulp is considerably increased by the addition of adenylic acid but is not influenced by added urea. The ammonia formation from the added nucleotide may reach 80—85% of the theoretical value. Even after brief electrical stimulation of the intact frog's muscle an increase in the ammonia value results, and after prolonged stimulation the ammonia may reach nine times its initial value.

A seasonal variation in the amount of the ammonia precursor in *Rana esculenta* has been demonstrated by G. Embden and H. Wassermeyer,[9] who find that a maximum is reached in May. After prolonged exercise by jumping, the ammonia content of the gastrocnemius removed from the intact frog is increased, whilst if a period of rest follows the exercise the ammonia decreases. The increase in ammonia following work is more easily demonstrated in *R. esculenta* than in *R. temporaria*, but if the latter animal is kept at an artificially increased temperature (26—27°) during the autumn, effects are obtained similar to those recorded in the case of the former animal in May. The reversibility of the formation of free ammonia in the isolated gastrocnemius of the frog has been investigated by G. Embden, M. Carstensen, and H. Schumacher.[10] The recombination process is most easily demonstrated in spring and summer frogs, whilst in winter the reversibility is greater, so that

[6] *Naturwiss.*, 1929, **17**, 546; *A.*, 1110.   [7] *Ann. Reports*, 1928, **25**, 256.
[8] *Z. physiol. Chem.*, 1928, **179**, 149; *A.*, 346.
[9] *Ibid.*, 1928, **179**, 161; *A.*, 346.   [10] *Ibid.*, p. 186; *A.*, 346.

it is difficult to show the initial increase under direct electrical stimulation unless this is so prolonged as to damage the muscle tissue and so interfere with the resynthesis. Nevertheless, by increasing the rate of stimulation it is possible to demonstrate the initial increase, the intervals between stimuli becoming too short to permit of recombination of the ammonia. That adenylic acid, and possibly adenosine, are the sole sources of the ammonia formed in those muscle processes is the conclusion of G. Embden and H. Wassermeyer,[11] who have investigated the composition of extracts from the hind limb muscles of the frog and from the biceps femoris of the rabbit. A relationship is found between the nitrogen of the copper–lime precipitates from such extracts and the free ammonia originally present in the extract. The sum of these two values is more or less constantly five times that of the ammonia nitrogen obtained after complete deaminisation by 2% sodium bicarbonate solution. The validity of the inference is considerably strengthened by further results from Embden's laboratory, published by G. Schmidt,[12] which demonstrate that adenylic acid from muscle and adenosine (which has not yet been shown to occur free in muscle) are easily deaminised by rabbit-muscle juice, whereas adenine, guanine, guanosine, and guanylic acid are unaffected. The ammonia production is due to two deaminases, one specific for adenylic acid, the other for adenosine. A highly active preparation of the former deaminase, with an optimum at p_H 5·9, was obtained by adsorption on aluminium hydroxide, from which the enzyme could be eluted by sodium phosphate solution. The adenosine deaminase remains in solution during the adsorption process.

Inosinic acid, the deaminisation product of the adenylic acid of muscle, was isolated in the course of these investigations.

Schmidt makes the rather remarkable observation that the adenylic acid of muscle differs from that of yeast, since the latter, unlike the former, is not attacked by the muscle deaminase. This observation is the subject of a further communication by G. Embden and G. Schmidt [13] in which it is stated that the physical constants of the two acids, as determined by observation of the specific rotations, melting points and mixed melting points, reveal definite differences. In addition to the difference in the behaviour of the two acids towards the muscle enzyme it is also found that the yeast acid is much more susceptible to acid hydrolysis than is the muscle acid. K. Pohle [14] records the isolation from ox-heart muscle of adenylic acid identical with that isolated from skeletal muscle.

It remains, in concluding our survey of this important series of

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[11] *Z. physiol. Chem.*, 1928, **179**, 226; *A.*, 346.   [12] *Ibid.*, p. 243; *A.*, 346.
[13] *Ibid.*, 1929, **181**, 130; *A.*, 591.   [14] *Ibid.*, 1929, **184**, 261; *A.*, 1329.

papers, to mention one further study from Embden's laboratory. In this, H. Wassermeyer [15] deduces from the electrometric titration curves of adenylic acid and of inosinic acid that the two acids are of comparable strength, since, although the latter acid is stronger than the former within the range of the first dissociation constant, this difference disappears in the range of the second dissociation constant. From this it is concluded that the ammonia formed during the contraction of the muscle tends to push the reaction towards the alkaline range. It is therefore clear that the process of ammonia formation may be an important part of the buffer mechanisms of the muscle.

The view that adenylic acid is the precursor of the ammonia of muscle is supported by J. K. Parnas,[16] who previously had stressed certain difficulties in the way of accepting it.[17] Parnas finds that in fresh muscle the purine bases are present chiefly as free nucleotides. In winter frogs the fresh muscle contains 82% of the purine nitrogen in the form of the adenine nucleus and 18% in the hypoxanthine nucleus, whilst in summer frogs the corresponding figures are respectively 89% and 11%. Mechanical injury transforms the greater part of the adenylic acid into inosinic acid. When ground for a few minutes, the muscle pulp gives 23% and 77% of purine nitrogen for the adenine and hypoxanthine nuclei respectively. In winter the deaminisation of the adenylic acid corresponds quantitatively to the traumatic formation of ammonia. Muscle stimulation under anaerobic conditions produces a conversion of adenine nuclei into hypoxanthine nuclei, equivalent to the ammonia production, but under aerobic conditions the ammonia production is greatly in excess. It is suggested that this may be due to the deaminisation of other substances leading to a resynthesis of adenylic acid from inosinic acid.

W. Mozolowski [18] still finds certain difficulties in accepting adenylic acid as the sole source of the ammonia which is formed in sterile blood on keeping. In part such ammonia arises from adenylic acid, but the deaminisation of this acid cannot account for the whole of it. None the less the purine content of the blood of various animals bears a close relationship to the extent of the ammonia formation; for instance, the blood of man, the pig and the rabbit contains greater quantities of purine bases than does the blood of the ox and horse, and greater quantities of ammonia are formed in the former than in the latter. In fresh blood the purine bases are present practically exclusively as nucleotides,

[15] Z. physiol. Chem., 1928, **179**, 238; A., 397.
[16] Biochem. Z., 1929, **206**, 16; A., 598.   [17] Ann. Reports, 1927, **24**, 258.
[18] Biochem. Z., 1929, **206**, 150; A., 588.

particularly adenylic acid. Free adenine is not found in the blood. During the formation of ammonia in the blood the adenylic acid is split with the formation of inosinic acid, and the latter is stated to be further broken down with the formation of free phosphoric acid.

Previous reference has been made to the failure to correlate the processes of traumatic formation of lactic acid and ammonia in muscle; [19] M. Lehnartz [20] has studied the process in the frog's gastrocnemius in isotonic and isometric contractions. It is found that the ammonia formation depends on the interval between successive stimuli. For instance, with 100 stimuli at 4-second intervals no formation of ammonia is detected, whereas with intervals of 1 second the ammonia formed is considerable.[21] The lactic acid/ ammonia ratio varies from 9—22 with 1-second intervals to infinity with longer intervals.

Pyrophosphate in Muscle.—In the Report of last year [22] reference was made to the demonstration by K. Lohmann of the presence of pyrophosphate in muscle. During the past year further observations on the occurrence and behaviour of pyrophosphate have been made by the same worker. The first [23] of this important series of papers gives in greater detail the results which were briefly described last year. In addition to the methods of identification to which reference was then made, the method of electrometric titration has been used and the resultant titration curves compared with those of authentic pyrophosphate. Quantitatively the biological pyrophosphate is determined as the difference between the " true " inorganic phosphate plus phosphagen phosphate, and the value obtained after seven minutes' further hydrolysis by means of N-hydrochloric acid at 100°.

Further investigation [24] has shown that pyrophosphate is widely distributed in Nature, being found in bacteria, yeast, pea seedlings, in the striated muscle of invertebrates and vertebrates, and in most of the organs of vertebrates. All cells which can utilise carbohydrates appear to contain this readily hydrolysable pyrophosphate.

In a further paper [25] the physiological behaviour of the pyrophosphate fraction is described. The pyrophosphate level of the intact frog's muscle in oxygen remains steady while resting for periods up to 20 hours and also during moderate stimulation. More severe stimulation produces some hydrolysis of the pyrophosphate to orthophosphate, whilst in heat and chloroform rigor almost all the pyrophosphate is hydrolysed. In a pulp of frog's

[19] *Ann. Reports*, 1928, **25**, 258.

[20] *Z. physiol. Chem.*, 1929, **184**, 183; *A.*, 1332.

[21] See also Embden, Carstensen, and Schumacher, p. 227.

[22] *Ann. Reports*, 1928, **25**, 250.   [23] *Biochem. Z.*, 1928, **202**, 466; *A.*, 208.

[24] *Ibid.*, 1928, **203**, 164; *A.*, 347.   [25] *Ibid.*, p. 172; *A.*, 347.

muscle or in a sodium bicarbonate–potassium chloride extract of the muscle the pyrophosphate is completely hydrolysed during autolysis at 40°, and 75% of the orthophosphate formed during this process arises from the pyrophosphate.

As has already been stated, all cells which utilise carbohydrate appear to contain pyrophosphate, yet the respiration and the degradation of the carbohydrate by the cell are not dependent on the pyrophosphate fraction. Pyrophosphate administered orally is excreted in the urine as orthophosphate within 24 hours.

Two further communications deal with the possible associations of pyrophosphate with other muscle-cell constituents. O. Meyerhof and K. Lohmann [26] find that some of the loosely combined iron of the muscle cell may be removed with the pyrophosphate, but it could not be decided whether the iron was combined with the pyrophosphate in the cell. More recently, K. Lohmann [27] has described the isolation of the pyrophosphate fraction through the barium salt. Neutral hydrolysis of the complex salt thus obtained results in the formation of pyrophosphoric acid and adenylic acid, whilst after brief treatment with hot dilute acid there are obtained two molecules of orthophosphoric acid, one molecule of adenine, and one of pentosephosphoric acid. In view of the importance now attached to adenylic acid in relation to muscle function, this suggested association of the nucleotide with the newly discovered pyrophosphoric acid gains added interest. Bearing in mind the wide natural distribution of pyrophosphate which the foregoing observations reveal, it is not surprising to find that H. D. Kay [28] records the widespread presence of pyrophosphatase in mammalian tissues, the distribution being similar to that of the orthophosphoric esterase.

Phosphagen.—Data continue to accumulate rapidly regarding the physiological behaviour of the creatinephosphoric acid constituent of muscle. Early in the year under review there appeared a lengthy paper by C. H. Fiske and Y. Subbarow [29] giving in detail results eagerly awaited since the original announcement by these workers of the discovery of the chemical nature of phosphagen.[30] Various methods are described for the isolation of creatinephosphoric acid from deproteinised muscle filtrates. In one of these the creatine phosphoric acid is obtained as the crystalline barium hydrogen salt, but the yield is only some 5% of the total labile (phosphagen) phosphorus of the original extract. Another method, in which the

[26] *Biochem. Z.*, 1928, **203**, 208; *A.*, 347.

[27] *Naturwiss.*, 1929, **17**, 624; *A.*, 1098.

[28] *Biochem. J.*, 1928, **22**, 1446; *A.*, 99.

[29] *J. Biol. Chem.*, 1929, **81**, 629; *A.*, 590.

[30] *Ann. Reports*, 1927, **24**, 256.

final product was isolated as the crystalline calcium hydrogen salt, $C_4H_8O_5N_3PCa,4H_2O$, gave a 70% yield, and this is interpreted as indicating strongly that the whole of the labile phosphorus is present as creatinephosphoric acid. The structure proposed for the compound is that already suggested by Meyerhof and Lohmann.[31]

Fiske and Subbarow find that the creatinephosphoric acid of muscle is hydrolysed when the muscle is stimulated, when the blood supply is cut off, and when lactic acid or potassium chloride is injected intravenously. The injection of creatine does not increase the concentration of the phosphagen in the muscle. The titration curve of the calcium hydrogen salt indicates a second acid dissociation constant, $p_{k'_2}$ 4·58, and since by the method of intravital staining the interior of the muscle cell is shown to be distinctly acid (Rous), it is concluded that the hydrolysis of creatinephosphoric acid during the muscular contraction is accompanied by the liberation of a large amount of base and consequently functions as a mechanism for neutralising acid.

Another important contribution to the study of creatinephosphoric acid has been made by D. Nachmansohn.[32] In this investigation the isometric coefficient, K_m, and the isometric–time coefficient, K_t, of the isolated muscle have been measured. The former coefficient is the tension developed in kilograms × muscle length in cm./phosphagen phosphoric acid split off in mg., whilst the latter coefficient has as an additional factor in the numerator the duration of the tetanus in seconds. K_t is about 15 for two-seconds tetanus, 32 for five-seconds, and 50 for ten-seconds. The anaerobic resynthesis for periods of tetanus of varying length is about 30% of the amount hydrolysed. In curarised muscle, even for tetanus of two seconds' duration, the K_t value is relatively high and changes little with length of period or number of stimuli. It falls with submaximal and increases with excessive stimulation. When the muscle is immersed in phosphate–Ringer solution, a synthesis of creatinephosphoric acid occurs in excess of the resting level and up to 95% of the creatine present. In single isometric contractions less phosphagen is decomposed at lower temperatures than at higher temperatures even though the tension developed and the lactic acid formed may be the same. The K_m value for 30 to 50 stimuli is 70—100 at 4° and 40—60 at 24°. Nachmansohn concludes that the extent of decomposition of phosphagen is closely related to the speed of excitation and carries his observations a stage further in a later communication [33] in which the relationship of the

[31] *Ann. Reports*, 1928, **25**, 253.

[32] *Biochem. Z.*, 1929, **208**, 237; *A.*, 843.

[33] *Ibid.*, 1929, **213**, 262.

process to the chronaxie of the muscle in the normal state and under various abnormal conditions is considered. The present position has also been summarised by O. Meyerhof [34] in similar terms.

In studying the effect of " training " on the muscle, *i.e.*, repeated faradisation in the intact animal, D. Ferdmann and O. Feinschmidt [35] find that there results a marked increase in the creatinephosphoric acid. On discontinuing the " training," the normal level is reached after 4 to 6 days. On the other hand, no change is noted in the pyrophosphoric acid or in the hexosephosphoric acid during the " training " period.

E. Lehnartz [36] has published an important paper which attempts to correlate the various synthetic and breakdown processes in which the active substances of the muscle participate. It is found that there is a considerable enzymic synthesis of creatinephosphoric acid in muscle press juice at a suitable slightly alkaline reaction. Parallel with this there is a breakdown of lactacidogen and pyrophosphoric acid. The adenylic acid ion is found to have a high degree of specificity for furthering the synthesis of pyrophosphoric acid, and under its influence the synthesis takes place more rapidly than in any other ionically stimulated chemical process in the muscle. Inosinic acid and adenosine are without influence on the synthetic process. This result is of interest in view of the suggested correlation (Lohmann) between adenylic acid and pyrophosphoric acid to which reference has already been made in the present Report.

Methylguanidine in Muscle.—The presence of methylguanidine in extracts from ox flesh was recorded nearly 25 years ago, and its isolation from muscle tissues generally and other tissues has been frequently accomplished since. The methods chiefly employed have involved the use of silver nitrate and barium hydroxide or other similar reagents, and the possibility of the base arising by secondary changes from creatine was therefore not excluded. The isolation of methylguanidine from muscle extracts by methods free from such objections is the subject of three papers by A. Smorodincev and A. N. Adova [37] and one by S. A. Komarov.[38] Since the former workers have isolated the base by direct precipitation with picric acid and, in somewhat poor yield, as the benzenesulphonate, and since the latter investigator records its isolation as the picrolonate from the phosphotungstate fraction of the muscle extract, it is considered to exist preformed in the muscle. Moreover, O. Flössner

[34] *Naturwiss.*, 1929, **17**, 283; *A.*, 844.
[35] *Z. physiol. Chem.*, 1929, **183**, 261; *A.*, 1193.
[36] *Ibid.*, 1929, **184**, 1; *A.*, 1337.
[37] *Ibid.*, 1929, **180**, 192; **181**, 77; **182**, 259; *A.*, 342, 589, 839.
[38] *Biochem. Z.*, 1929, **211**, 326; *A.*, 1329.

and F. Kutscher [39] record its presence along with adenine in the urine of athletes. The best yield of the base obtained by Komarov was 0·06 g. per kilogram of fresh ox muscle, which is not regarded as comprising the total amount present, whilst Smorodincev and Adova obtained 0·0134% from dog muscle.

The Phosphatase of Bone.

The description by M. Martland and R. Robison [40] of the preparation and use of the phosphatase of ossifying bone, the existence of which was first revealed a few years ago,[41] will be welcomed in view of the usefulness of this powerful enzymic weapon. The enzyme is best prepared from the bones of young growing rachitic rats by extraction with chloroform water during 7—10 days, the bones having first been split longitudinally and the marrow removed. Evaporation of the filtered extracts over sulphuric acid in evacuated desiccators yields a dry residue weighing 5—8 mg. per c.c., no loss of activity occurring during the drying process. Purification can be effected by various methods; for instance, an inactive protein present in the dried residue may be precipitated at its isoelectric point (p_H 5·8), the enzyme may be precipitated with a mixture of alcohol and ether, or resort may be had to dialysis or ultrafiltration. No evidence of the existence of a co-enzyme for the bone phosphatase could be obtained.

The Hydrolysis of Hexosediphosphoric Acid by Bone Phosphatase.— The phosphatase preparation described in the foregoing has been used by Martland and Robison [42] to free the sugar component of the hexosediphosphoric acid of yeast from its phosphate groups. It will be recalled that the yeast diphosphoric acid has been identified by Morgan and Robison [43] as γ-fructose-1 : 6-diphosphoric acid, and on the removal of the phosphate groups the sugar should change to the equilibrium mixture of the α- and β-stereoisomerides of fructose having $[\alpha]_{5461}$ —111°. The free sugar obtained by Martland and Robison, even when the hydrolysis was conducted at p_H 7, showed a specific rotation of —76°, and under other conditions of reaction variable but likewise low results were obtained. In view of the now recognised rôle of phosphoric acid in achieving transformations of carbohydrates during the hydrolysis and synthesis of the esters formed by these two compounds, this result, in the opinion of the Reporter, in no way invalidates the earlier conclusions of Morgan and Robison regarding the structure of hexosediphosphoric acid.

[39] *Z. Biol.*, 1928, **88**, 382; *A.*, 466.
[40] *Biochem. J.*, 1929, **23**, 237; *A.*, 603.
[41] *Ibid.*, 1923, **17**, 286; *A.*, 1923, i, 730.
[42] *Loc. cit.*   [43] *Ann. Reports*, 1927, **24**, 252.

The structure originally suggested is supported by further evidence brought forward by Morgan.[44] It is shown that when the methyl hexosidediphosphoric acid is formed under conditions which favour the formation of the amylene-oxidic or stable configuration, none the less the product obtained is found to be the butylene-oxidic or reactive modification, and from this it is inferred that the 6-position is esterified with phosphoric acid, thus preventing any possibility of the production of the amylene-oxide ring even under conditions favourable to its formation.

The Hexosemonophosphoric Acid of Yeast.

The nature of the hexosemonophosphoric acid first isolated from yeast fermentations by Robison has not yet been fully elucidated. Apart altogether from the possible presence in the monophosphoric acid of the interesting trehalosemonophosphoric acid obtained by Robison and Morgan and described in the Report of last year,[45] it seems highly probable that the residual monophosphoric acid is not homogeneous. This view is strongly supported by certain results, as yet incomplete, of R. Robison and E. J. King,[46] from which it may be deduced that the main component is an aldose, almost certainly glucosemonophosphoric acid. This component is regarded by P. A. Levene and A. L. Raymond [47] as γ-glucose-5-phosphoric acid :

$$\mathrm{CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot CH \cdot CH(O \cdot PO_3H_2) \cdot CH_2 \cdot OH.}$$
$$\underline{\qquad\qquad O \qquad\qquad}$$
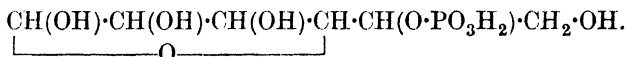
This conclusion is reached on the basis of the rate of hydrolysis of the methylglucosidic compound formed from the free acid in acid methyl alcohol at room temperature. The observed rate is that of a substance possessing the γ-lactal or butylene-oxidic structure. The phosphoric acid group cannot therefore be regarded as being attached to position 4. It is considered that position 6 is excluded, since the osazone of the Robison ester differs from that of the Neuberg ester (which is fructose-6-monophosphate). It is to be noted, however, that the method of glucoside formation employed by Levene and Raymond would lead to the production of the γ-lactal product should the hydroxyl group of position 4 be free to condense. Moreover, E. J. King and W. T. J. Morgan [48] have

[44] Report of the Meeting of the Biochemical Society (Feb. 4th), *J. Soc. Chem. Ind.*, 1929, **48**, 144.   [45] *Ann. Reports*, 1928, **25**, 247.

[46] Report of the Meeting of the Biochemical Society (Feb. 4th), *J. Soc. Chem. Ind.*, 1929, **48**, 143.

[47] *J. Biol. Chem.*, 1929, **81**, 279; *A.*, 423.

[48] Report of the Meeting of the Biochemical Society (Feb. 4th), *J. Soc. Chem. Ind.*, 1929, **48**, 143.

shown that by suitably varying the conditions of the condensation it is possible to obtain both γ- and δ-lactal products, *i.e.*, both the butylene- and the amylene-oxidic glucosides. In this case both positions 4 and 5 must be free. In a later communication King and Morgan [49] review all the available evidence and conclude that the most probable structure of the aldose ester constituent of the hexosemonophosphoric acid is that of glucose-3-monophosphoric acid :

$$\underset{\underline{\hspace{3cm} O \hspace{3cm}}}{CH(OH){\cdot}CH(OH){\cdot}CH(O{\cdot}PO_3H_2){\cdot}CH(OH){\cdot}CH{\cdot}CH_2{\cdot}OH}$$

The essential evidence upon which this conclusion is based is as follows : positions 1 and 2 are excluded, since an osazone is formed without loss of the phosphate group; positions 4 and 5, on the grounds mentioned above; position 6, on the same grounds as those brought forward by Levene and Raymond.[50] Position 3 therefore alone remains for the attachment of the phosphoric acid group. This argument is of course based upon the acceptance of the γ-fructose-1 : 6-diphosphoric acid structure for the yeast diphosphate, and the assumption, for which good evidence exists,[51] that the yeast monophosphate is essentially a glucose derivative. Should either of these views be modified as a result of future investigations, the arguments considered above will require to be recast.

The Processes of Bone Formation.

Bone and ossifying cartilage have been shown to contain a phosphatase,[52] and this enzyme is regarded as playing an active part in the processes of ossification by effecting the hydrolysis of certain phosphoric esters which H. D. Kay and R. Robison [53] and M. Martland and R. Robison [54] have shown to be present in the blood. The concentration of inorganic phosphate in the tissue fluid is thereby raised so that calcium phosphate is deposited. In support of this hypothesis evidence was furnished that the phosphatase is secreted in the region of the osteoblasts and hypertrophic cartilage cells. When severely rachitic bones were immersed in solutions of calcium hexosemonophosphate or calcium glycerophosphate, deposition of calcium phosphate took place in the periosteum and in the matrix of the proliferating and hypertrophic cartilage, but, on the other hand, no deposit was observed in the

[49] Report of the Meeting of the Biochemical Society (Mar. 15th), 1929, **48**, 296.

[50] *Loc. cit.*

[51] See J. Pryde and E. T. Waters, *Biochem. J.*, 1929, **23**, 573; *A.*, 952.

[52] *Ann. Reports*, 1923, **20**, 189.   [53] *Ibid.*, 1924, **21**, 197.

[54] *Biochem. J.*, 1926, **20**, 847; *A.*, 1926, 968.

small-celled cartilage of the epiphysis (R. Robison and K. M. Soames).[55] Similarly it was shown, by examining the cartilages and bones of human embryos and young infants that, although the ossified portions of young normal bones contained phosphatase in high degree, the non-ossifying cartilage was in all cases devoid of the enzyme (M. Martland and R. Robison).[56] H. B. Fell and R. Robison [57] have published an important paper which continues the investigations briefly outlined in the foregoing. The interest of this study, both from the point of view of technique and of results, is such that a detailed review is justified. The object has been to correlate the growth, development and phosphatase activity of isolated early embryonic femora and of undifferentiated limb-buds cultivated *in vitro*, and to compare these processes in the explants with the corresponding processes in the normal embryonic limb.

When explanted *in vitro* by a technique which is carefully described, the femur of the embryo chick at an early stage in development is completely deprived of a vascular system, nervous connexions, adjacent skeletal structures and of association with the limb musculature. Nevertheless, it is shown that the explant during cultivation *in vitro* is able to continue its anatomical development on the same general lines as in the normal limb, and at the same time undergoes a histological differentiation which is correlated with at least one of the chemical activities of the normal ossifying cartilage. The femora cultivated *in vitro* differed from the normal embryonic femora of the same age mainly in their much smaller size, in having relatively larger epiphyses, in the absence of a marrow cavity, and in being encased by a considerably thinner and more compact sheath of periosteal bone. All these differences may be attributed, in part at least, to the absence of certain mechanical and nutritional factors normally supplied by the blood. An interesting contrast was observed between the histological development *in vitro* of the 6-day femora and the 3-day limb-buds. No differentiation into structures corresponding to the epiphysis and diaphysis took place in the cartilage formed from originally undifferentiated 3-day mesenchyme. On the other hand, the explanted 6-day femora which, at the time of explantation were composed of very simple early cartilage, developed epiphyses and diaphyses during the same period of cultivation. Thus under the conditions of the experiments, the self-differentiating capacity of the 6-day femur was considerably greater than that of the 3-day limb-bud.

It is shown that the femora, entirely devoid of phosphatase when

[55] *Biochem. J.*, 1924, **18**, 740; *A.*, 1924, i, 904.

[56] *Ibid.*, p. 1354; *A.*, 1925, i, 201.

[57] *Ibid.*, 1929, **23**, 767; *A.*, 1197.

removed from the 6-day embryo, synthesise the enzyme during cultivation *in vitro* and that the production of the phosphatase follows very closely the progress of histological differentiation in the cartilage. For instance, the first appearance of phosphatase in the explanted 6-day femora, after 3 days' cultivation, coincided with the first appearance in the cartilage of a zone of enlarged cells. The extension of this zone and increased enlargement of the cells in the later cultures were accompanied by a corresponding increase in the amount of phosphatase. The parallelism between enzyme synthesis and histological differentiation is most clearly shown by considering the ratio of phosphatase to the dry weight of the femur (A/W). With the increasing proportion of hypertrophic cells and the gradual development of periosteal bone observed up to the twenty-first day of cultivation, there was found an increase in the value of A/W from zero to a maximum of 0.35. The degeneration which was observed in the 24-day, and still more extensively in the 27-day cultures, was accompanied by a halt in the increase of this ratio, followed by a fall to the value 0.26 at 27 days. Further evidence of this parallelism was provided by the chance inclusion in the series of one culture (15-day) in which, for some reason, the histological differentiation was very backward and for which the value A/W proved to be correspondingly low. On the other hand, it was shown that the cartilage formed during cultivation of 3-day embryonic limb-buds is entirely of the small-celled (undifferentiated) type and that even after 21 days' cultivation this cartilage synthesises no phosphatase. From the results of these remarkably interesting investigations Fell and Robison conclude that in the development of skeletal tissue *in vitro* phosphatase is synthesised by cartilage only if hypertrophic cells are present.

During the year under review, certain other interesting observations on the chemistry of calcification have appeared. N. W. Taylor and C. Sheard [58] have investigated by X-ray diffraction patterns and by optical methods several types of calcified tissues, including normal bone, dental enamel, rachitic bone, bone low in phosphorus, and salivary and tubercular calculi, and find that the solid inorganic phase consists essentially of very small crystals of apatite minerals of the general formula $3Ca_3(PO_4)_2,CaX_2$, where X_2 ordinarily represents CO_3, F_2, $(OH)_2$, O, SO_4, and Ca which may to some extent be replaced by Mg. The typical minerals of this formula are podolite, dahllite and fluorapatite. No evidence of the presence of brushite, $CaHPO_4,2H_2O$, was obtained either in normal or in pathological deposits. On the other hand, M. J. Shear, M. Washburn, and B. Kramer [59] still regard the composition of bone

[58] *J. Biol. Chem.*, 1929, **81**, 479; *A.*, 463.   [59] *Ibid.*, 1929, **83**, 697; *A.*, 1326.

as an open question and state that the presence of $CaHPO_4$ in bone generally, and in primary calcification especially, should not be overlooked. R. Klement [60] has published data which lead him to the conclusion that the inorganic portion of bone consists principally of a basic calcium phosphate of the composition $3Ca_3(PO_4)_2,Ca(OH)_2$, with inclusions of alkaline-earth carbonates and alkali bicarbonates. B. Kramer, M. J. Shear, and M. R. McKenzie [61] find no deviation from the normal in the ratio of the residual calcium to phosphorus of the bones of growing rats as a result of the administration of massive doses of irradiated ergosterol (see also p. 251). On the other hand, C. G. Lambie, W. O. Kermack, and W. F. Harvey [62] state that the administration of parathyroid hormone to rats appears to cause a change in the form in which calcium exists in the bones.

Specific Carbohydrates and Immunology.

In the Report for 1926 there was summarised the progress achieved in elucidating the rôle of specific carbohydrates in immunological reactions. Further reference to this interesting field is necessitated by recent publications from the American school which is particularly associated with its development. W. F. Goebel and O. T. Avery,[63] with the view of coupling known sugar residues with proteins of ascertainable antigenic properties, have synthesised p-aminophenol-β-glucoside and p-aminophenol-β-galactoside and have coupled these, after diazotisation, with globulins and albumins. They have obtained the following four protein–sugar complexes : phenol-β-glucosideazoglobulin, phenol-β-galactosideazoglobulin, phenol-β-glucosideazoalbumin, and phenol-β-galactosideazoalbumin. These are referred to as gluco- or galacto-globulins and -albumins respectively. The steps employed in the synthesis were as follows. Acetobromohexose, prepared from the penta-acetyl compound, was condensed with silver p-nitrophenoxide and after de-acetylation of the condensation product there was obtained p-nitrophenol-β-hexose; this was reduced to the p-aminophenol compound by hydrogenation in the presence of a platinum catalyst : coupling with the protein was achieved in the usual way by means of sodium nitrite and hydrochloric acid at $0°$. In the case of the globulin compounds the glucose–protein contained 17% of reducing sugar and the galactose–protein 10%.

The immunological reactions of these sugar–protein compounds have been investigated by O. T. Avery and W. F. Goebel [64] and it

[60] *Z. physiol. Chem.*, 1929, **184**, 132; *A.*, 1328.
[61] *J. Biol. Chem.*, 1929, **82**, 555; *A.*, 960.
[62] *Nature*, 1929, **123**, 348; *A.*, 475.
[63] *J. Exp. Med.*, 1929, **50**, 521.   [64] *Ibid.*, p. 533.

is found that, when two chemically different carbohydrate deriv-atives are bound to the same protein, the resulting antigens exhibit distinct immunological specificity. On the other hand, when the same carbohydrate radical is conjugated with two chemically different and serologically distinct proteins, both of the sugar proteins formed acquire a common serological specificity. Thus the newly acquired specificity of the artificially prepared sugar–proteins is determined by the chemical nature of the carbohydrate radical. The simple differences in the molecular configuration which distinguish the two isomerides glucose and galactose suffice to orient protein specificity when the two sugars are coupled to the same protein. The uncon-jugated glucosides, although they are not themselves precipitable in the serum from animals immunised with the homologous sugar–protein, nevertheless inhibit in a specific manner the reaction between the homologous sugar–protein and its specific anti-body. The sugar compounds unattached to proteins are non-antigenic but specific-ally reactive, as is shown by these inhibition tests. These simple artificially prepared glucosidic compounds are therefore placed in the class of carbohydrate haptenes, the most conspicuous examples of which are the specific polysaccharides naturally found in certain micro-organisms.

In another communication W. S. Tillett, O. T. Avery, and W. F. Goebel [65] give the results of a study of the active and passive anaphylaxis induced by the sugar–proteins in guinea-pigs. When these animals are passively sensitised with the serum of rabbits immunised with the gluco-globulin, they exhibit typical anaphylactic shock when subsequently inoculated with gluco-albumin, whilst the serum of rabbits immunised with galacto-globulin similarly sensitises guinea-pigs to galacto-albumin. Guinea-pigs actively sensitised with the sugar–proteins are also subject to anaphylactic shock when injected after 2 days with sugar–proteins containing the same carbohydrate radical as that present in the sensitising antigen, regardless of the kind of protein with which it is combined. The unconjugated glucosides, although themselves not capable of inducing shock, will inhibit the anaphylaxis if injected prior to the introduction of the toxigenic sugar–protein, and if the carbohydrate is the same as that combined in the sugar–protein molecule. These results appear to the Reporter to be extremely suggestive and far-reaching in their implications and the success of this direct attack on the apparently complicated problems of immunology is indeed very gratifying.

A further highly interesting observation in this field has been made by M. Heidelberger, O. T. Avery, and W. F. Goebel,[66] who

[65] *J. Exp. Med.*, 1929, **50,** 551.   [66] *Ibid.*, 1929, **49,** 847; *A.*, 1201.

find that by partial acid hydrolysis of gum-arabic in the cold there is obtained an immunologically specific carbohydrate comparable in its precipitating activity for Types II and III antipneumococcus sera with the bacterial soluble specific substances themselves. On further hydrolysis the carbohydrate yielded galactose and two or more complex sugar acids, one of which appeared to be an aldobionic acid similar to those isolated from the specific polysaccharides of the Type III pneumococcus and the Type A Friedländer bacillus. This acid was subsequently obtained in a crystalline condition by M. Heidelberger and F. E. Kendall,[67] who provisionally ascribe to it the structure of α- or β-glucurono-3- or -6-α-galactose.

A. Stull [68] finds that the specific soluble carbohydrate of Type III pneumococcus described by Heidelberger, Goebel, and Avery [69] can be isolated from an unbuffered culture medium after 18 hours of growth. The whole of the specific carbohydrate, which was the only specific precipitating material found, was contained in the distilled water extract of the fat-free material. J. Fürth and K. Landsteiner [70] find that from the main serological types of the typhoid-paratyphoid groups of organisms specific precipitable substances can be obtained. Pronounced chemical differences were not observed, but the substances are rich in carbohydrates and contain very little protein. Small quantities of a material apparently of a fatty nature were detected.

The Molecular Weight of Hæmoglobin.

An interesting application of the diffusion coefficient of a substance in solution to the calculation of the radius and weight of the particle has been made by J. H. Northrop and M. L. Anson,[71] who have calculated, with the help of the Einstein equation, the molecular weight of carbon monoxide–hæmoglobin. It has been found that the difficulties inherent in determining the diffusion coefficient of a slow-moving substance of large molecular dimensions could be overcome if the rate of diffusion was accelerated by allowing the process to occur through a thin porous plate between two solutions of different concentrations. Suitable plates were prepared from sintered porous Jena glass or from alundum. The constant of the apparatus is found by standardising it with a substance of known diffusion coefficient, after which the required diffusion coefficient, D, can be obtained. The Einstein equation, $D = RT/6\pi Nr\eta$, in which N is Avogadro's number, η the viscosity of the

[67] J. Biol. Chem., 1929, 84, 639.   [68] Ibid., 1929, 82, 641; A., 958.
[69] Ann. Reports, 1926, 23, 248.
[70] J. Exp. Med., 1929, 49, 727; A., 1200.
[71] J. Gen. Physiol., 1929, 12, 543; A., 587.

liquid, and r the radius of the molecule, then permits of the calculation of the molecular weight. The specific gravity was assumed to be the same as that of solid hæmoglobin, and from the observed diffusion coefficient, 0.0420 ± 0.0005 cm.^{2} per day at 5°, the molecular weight of carbon monoxide–hæmoglobin is calculated to be 68,500 $\pm$ 1,000. This figure agrees within the experimental error with that of 67,000 found by Adair [72] by osmotic pressure measurements, and of 68,000 found by Svedberg [73] from experiments on the rate of sedimentation produced by very rapid centrifuging.

Hæmochromogens.

Several important publications dealing with hæmochromogen and related compounds have appeared during the past year. M. L. Anson and A. E. Mirsky [74] have made a study of the compounds formed by reduced hæmatin and cyanide. One of these is found to be a typical hæmochromogen and to it the name cyanohæmochromogen has been given. It probably contains one cyano-group to each molecule of hæmatin. The hæmochromogen formed from hæmoglobin is a compound of denatured globin and reduced hæmatin, one molecule of the former being able to convert ten molecules of reduced hæmatin into hæmochromogen. It is found that edestin and zein are less efficient as bases in the formation of hæmochromogens than is denatured globin. R. Hill [75] finds that hæmochromogens generally are formed by the union of the reduced hæmatin molecule with two molecules of the nitrogenous substance. This is supported by data derived from a study of the pyridine, nicotine, and cyanide compounds of reduced hæmatin. The new cyanohæmochromogen described by Anson and Mirsky, [76] which these workers found to contain one molecule of alkali cyanide to each molecule of reduced hæmatin, is shown to be analogous to the carbon monoxide compound of reduced hæmatin. It combines with a second molecule of cyanide to form a true hæmochromogen, or with one molecule of nicotine to form a mixed nicotine–cyanohæmochromogen. The name " cyano-reduced hæmatin " is proposed for it and the previously suggested name of cyanohæmochromogen is transferred to the hæmochromogen containing two molecules of cyanide described by Hill himself.

The linking between the protein and the prosthetic group in hæmoglobin has been studied by F. Haurowitz and H. Waelsch, [77]

[72] *Ann. Reports*, 1926, **23**, 251.

[73] *Ibid.*, 1924, **21**, 263; *Z. physikal. Chem.*, 1927, **127**, 51; *A.*, 1927, 716.

[74] *J. Gen. Physiol.*, 1928, **12**, 273; *A.*, 87.

[75] *Proc. Roy. Soc.*, 1929, *B*, **105**, 112; *A.*, 1094.

[76] *Loc. cit.*

[77] *Z. physiol. Chem.*, 1929, **182**, 82; *A.*, 713.

who confirm the findings of Hill and Holden [78] concerning the formation of a true hæmoglobin, capable of absorbing molecular oxygen, from native globin and hæmin. In similar manner, coupling was observed between native globin and dimethyl meso-hæmin and with reduced hæmin. It is therefore considered that the unsaturated side chains and carboxyl groups of hæmin do not participate in the linkage with globin. Haurowitz and Waelsch could not, from their spectroscopic observations, find any evidence for coupling between globin and hæmatoporphyrin (Nencki) (compare Hill and Holden, *loc. cit.*).

Cytochrome and Respiratory Enzymes.—In previous Reports [79] attention has been directed to the fundamental work of D. Keilin on cytochrome. A further publication by the same author [80] deals with the close association which exists between this respiratory pigment and the oxidase systems of the cell. Earlier work has established the presence in all aerobic organisms of cytochrome with its three hæmatin compounds a', b', and c', and of an unbound hæmatin compound similar to the protoporphyrin of hæmoglobin. Of these four hæmatin compounds, the components a' and c' of cytochrome are not autoxidisable, whilst b' of cytochrome (in washed muscle and dried yeast cells) and the unbound hæmatin are autoxidisable, and the last in the reduced state combines with carbon monoxide. The hæmochromogen precursor of cytochrome is also autoxidisable, but does not combine with carbon monoxide. These hæmatin compounds are responsible for the thermostable peroxidase reaction of the cell, a reaction which is revealed by the oxidation of various chromogens such as benzidine, guaiacum and p-phenylene-diamine in the presence of hydrogen peroxide. The cells of yeast, muscle, and other tissues also contain an insoluble thermolabile indophenol oxidase which is responsible for the oxidation of cyto-chrome, especially of its non-autoxidisable a' and c' components, as the oxidation of cytochrome is inhibited or abolished by the same factors which inhibit or abolish the activity of the indophenol oxidase. Cytochrome in the living cell is reduced by various organic molecules (metabolites) which, being activated by dehydrases, become hydrogen donators. All factors which inhibit the activity of the dehydrase system of the cell, such as narcotics, warming to 52°, and very low temperatures also delay the reduction of oxidised cytochrome. It is therefore concluded that cytochrome acts as a carrier between two types of activating mechanisms in the cell : (*a*) the dehydrases activating the hydrogen of organic molecules,

[78] *Ann. Reports*, 1927, **24**, 265.

[79] *Ibid.*, 1925, **22**, 238; 1926, **23**, 251; 1927, **24**, 268.

[80] *Proc. Roy. Soc.*, 1929, *B*, **104**, 206; *A.*, 470.

and (*b*) the indophenol oxidase activating oxygen.   Cytochrome thus acts as a hydrogen acceptor which is specifically oxidised by the indophenol oxidase.   It is thought that the autoxidisable hæmatin compounds, *b'* of cytochrome, unbound hæmatin, and the hæmochromogen precursor of cytochrome may also act as carriers between the hydrogen donators and molecular oxygen, and also as direct catalysts promoting the oxidation of substances which are not activated by specific dehydrases.

Synthetic Porphyrins.—No attempt can be made here to review adequately the considerable volume of work on synthetic porphyrins and related compounds which continues to appear from the German laboratories, but it is felt that some reference to the synthesis of hæmatoporphyrin, protoporphyrin, and hæmin by H. Fischer and K. Zeile [81] will be welcomed by the biochemist.   When an absolute alcoholic solution of diacetyldeuteroporphyrin [82] and potassium hydroxide is boiled, hæmatoporphyrin is obtained.   Its hydrochloride is crystallographically and spectroscopically identical with natural hæmatoporphyrin hydrochloride.   At 105° in a high vacuum the free hæmatoporphyrin passes almost quantitatively into protoporphyrin identical with that derived from blood.   The synthetic hæmatoporphyrin hydrochloride is converted by hydrogen iodide in glacial acetic acid into mesoporphyrin.   From the synthetic protoporphyrin, hæmin, $C_{34}H_{32}O_4N_4ClFe$, has been prepared.   It is identical with natural hæmin.   At the present stage of these investigations H. Fischer regards the following as the most satisfactory formula for hæmin :
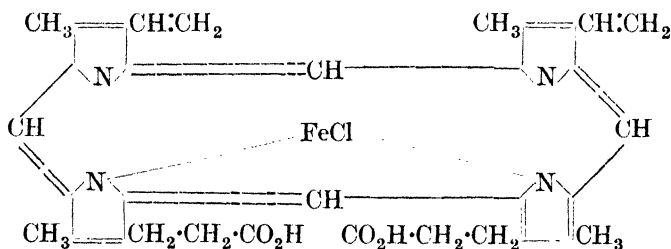
The formation of porphyrins in living organisms is the subject of two papers to which reference will be made in concluding this section of the Report.   H. Fink [83] in a lengthy communication deals with the accumulation of coproporphyrin in yeasts cultured over a long period.   In all the yeasts the spectrum of cytochrome was recognisable, and the accumulation of the porphyrin did not kill the

[81] *Annalen*, 1929, **468**, 98; *A.*, **333**.   [82] *Ann. Reports*, 1927, **24**, 270.
[83] *Biochem. Z.*, 1929, **211**, 65; *A.*, 1340.

yeasts, nor did it alter the type of their metabolism. A. A. H. van den Bergh [84] records the excretion by a patient suffering from congenital porphyrinuria of coproporphyrin identical with that synthesised by H. Fischer from ætioporphyrin III.[85]

The Chemistry of the Fat-soluble Vitamins.

In the field of the fat-soluble vitamins many interesting results have accumulated during the past year. The main interest of workers in this field has been directed towards the following four problems : (a) the possible identity of vitamin-A with the hydrocarbon carotin, (b) the specificity of the arsenic and antimony trichloride tests for vitamin-A, (c) the chemical relationship of vitamin-D with ergosterol and its derivatives, and (d) the question of " hypervitaminosis " as a result of the excessive administration of vitamin-D preparations. These questions will be considered seriatim.

*Vitamin-*A *and Carotin.*—Carotin is a coloured hydrocarbon of plant origin having the formula $C_{40}H_{56}$. Its constitution is not yet fully elucidated, but it appears to possess 11 double bonds, of which 8 are probably conjugated.[86] The question of the possible identity of this interesting hydrocarbon with the vitamin has received previous consideration mainly by Steenbock and his collaborators in America and by Drummond in this country,[87] and from the evidence then accumulated it seems not unnatural that the question of possible identity should have been dismissed. The discussion has been reopened by B. von Euler, H. von Euler, and H. Hellström,[88] who point out that in previous biological tests of the vitamin-A activity of the carotinoid pigments, no provision was made for the presence of vitamin-D in the diet and the results obtained by the earlier investigators are not regarded as trustworthy. It is true that in the earlier work growth-promoting activity was occasionally detected, but this was then ascribed to the presence of the vitamin as a contaminant of the carotin. Before the results published during the past year by other workers are considered, those of von Euler and his associates will first be reviewed. B. von Euler, H. von Euler, and P. Karrer [89] find that the addition of daily doses of purified carotin to the basic diet of rats in amounts of 0·10 to 0·03 mg. produces an increase in growth comparable with that

[84] *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 15; *A.*, 596.

[85] *Ann. Reports*, 1927, **24**, 270.

[86] L. Zechmeister, L. von Cholnoky, and (Frl.) V. Vrabély, *Ber.*, 1928, **61**, [*B*], 566; *A.*, 1928, 524.

[87] *J. Biol. Chem.*, 1921, **46**, *Proc.* xxxii; *Biochem. J.*, 1919, **13**, 81.

[88] *Biochem. Z.*, 1928, **203**, 370; *A.*, 358.

[89] *Helv. Chim. Acta*, 1929, **12**, 278; *A.*, 610.

obtained with vitamin-A.   Pure carotin and the isomeric carotinoid lycopin (found in tomatoes) give the Rosenheim–Drummond antimony trichloride colour reaction, and when the liver extracts of the carotin-fed rats were tested colour intensities were obtained similar to those given by the livers of normally fed rats.   The growth-promoting effect is not general to all carotinoids, since negative growth results were obtained with lycopin and its carboxylic acid, and with xanthophyll, α-crocetin, bixin, and capsanthin. These pigments, it is to be noted, give the antimony trichloride reaction.   Positive growth effects were obtained with dihydro-α-crocetin if vitamin-D in the form of irradiated arachis oil was fed at the same time.   Further results of a similar nature are published in a later paper by H. von Euler, P. Karrer, and M. Rydbom.[90]   In addition to the compounds already mentioned, growth tests were carried out on the following carotinoid derivatives with negative results : norbixin, dehydronorbixin, fucoxanthin, and dihydro-α-crocetin methyl ester.   Carotin with a melting point of 182—183° fed to rats in daily doses of 0·03 mg. produced continuous growth. It is admitted that the nature of the preparation does not exclude the possibility of the presence in the carotin of a very active substance, but on the other hand the purest carotin preparations are the most active vitamin-A preparations yet obtained.   Carotin from stinging nettles is found to be slightly less active than that from carrots and it is argued that if accompanying impurities are responsible for the biological activity they do not occur solely in the carrot. Di-iodocarotin was found to be active and it is thought that it is not the carotin derivative itself but a product derived from it after resorption which is the growth-promoting substance.   Results obtained with lutein appear to be variable, but a recent paper by H. von Euler and H. Hellström [91] states that it exhibits specific growth-promoting properties.   B. von Euler, H. von Euler, and P. Karrer [92] have made a histological examination of the epiphyses of rats kept on a diet containing both carotinoid material and sufficient amounts of vitamin-D.   Growth continues but bone formation is deficient.   In rats which have received more than the minimum necessary amount of carotin the excess accumulates in the liver.

D. L. Collison, E. M. Hume, I. Smedley-Maclean, and H. H. Smith [93] have examined the vitamin-A substance of green spinach, cabbage leaves, and of carrots, and find that it is contained in the

[90] *Ber.*, 1929, **62**, [*B*], 2445; *A.*, 1343.
[91] *Biochem. Z.*, 1929, **211**, 252; *A.*, 1334.
[92] *Ibid.*, 1929, **209**, 240; *A.*, 1112.
[93] *Biochem. J.*, 1929, **23**, 634; *A.*, 1202.

most highly unsaturated fraction of the unsaponifiable matter. As far as the process of purification employed by them extended, it remained associated with the carotin crystals. Carotin was separated in a crystalline condition from all three sources and while no claim is made that the specimens obtained were of a high degree of purity, none the less the vitamin-A activity of the specimens of highest melting point (174—178°; from the cabbage material) was not less than that shown by specimens of lower melting point (163—164°; from spinach). It is suggested that the presence of fat in the diet or of something in the unsaponifiable fraction of the fat is possibly necessary for the utilisation of carotin. The association of vitamin-A activity with carotin in the carrot has been investigated by T. Moore,[94] who, using a basal diet containing vitamin-D in the form of irradiated ergosterol in arachis oil, finds that a daily dosage of 100 mg. of fresh carrot sufficed to cure xerophthalmia and to restore good growth in rats deprived of vitamin-A. Carrot fat from which much of the carotin had been removed was active in doses of 0·4 mg. daily, whilst carotin itself (m. p. 174°), recrystallised many times, was found to be active in doses of 0·01 mg. daily.

The foregoing data certainly strongly suggest that chemically pure carotin can restore growth in rats suffering from deficiency of vitamin-A. None the less, the Swedish workers appear to consider that it is improbable that the vitamin-A of cod-liver oil is carotin itself and the suggestion has been put forward that several substances possessing the physiological activity of the vitamin might exist. The vitamin-A of cod-liver oil, for example, might be derived from the carotinoids of marine algæ. Von Euler and his associates have indeed suggested that the vitamin-A activity is not the property of any single substance but is due to the presence in various molecules of the " polyene " grouping, a system of double bonds which gives rise to colour reactions and which is held to possess catalytic powers in $vivo$. It has been stated in the foregoing that von Euler, von Euler, and Karrer find that excess carotin accumulates in the liver, but on the other hand a recent note by T. Moore [95] suggests that carotin does not accumulate as such in the liver, although there is a marked increase in the vitamin-A content as measured by the antimony trichloride reaction. A somewhat similar result has been recorded by L. S. Palmer,[96] who states that pig's liver contains a minute quantity of an unsaponifiable pigment, soluble in light petroleum, which strongly resembles carotin in solubility and in adsorption properties and gives some of the colour

[94] *Biochem. J.*, 1929, **23**, 803; *A.*, 1202.
[95] *Lancet*, 1929, ii, 380; *A.*, 1343.
[96] *Amer. J. Physiol.*, 1929, **87**, 553; *A.*, 463.

reactions, but not others, given by carotinoids. From a qualitative and a quantitative study of its spectroscopic properties it is concluded that the liver pigment cannot be carotin. It will be obvious from the following section of this Report that arguments based on colour tests must be employed with discretion, but it is by no means inconsistent with the present trend of work on vitamin-A that carotin and closely related substances are capable of forming the vitamin which subsequently may accumulate in the liver.

*The Colour Reaction for Vitamin-*A.—A considerable amount of work has recently appeared relating to the applicability of the Rosenheim–Drummond colour reaction for vitamin-A. J. C. Drummond and R. A. Morton [97] have subjected it to a critical examination in parallel with biological and spectrographic tests on cod-liver oil. They rightly stress the considerable variations in the biological method in view of the individual nature of the responses of many animals, and state that quantitative differences of less than 100% in vitamin-A potency cannot be detected with certainty by the biological method. On the other hand, the relative values obtained by all three methods were in agreement, and in particular the agreement between the colorimetric and the spectrographic method was very close. As far as cod-liver oil is concerned, these workers unhesitatingly recommend the colorimetric method of assay, and Professor Drummond states that in what is admittedly a very wide range of experience no single case has been encountered in which there has been disagreement between the animal tests and the intensity of the blue colour showing maximum absorption near 608 $\mu\mu$. In regard to the spectrographic test (intensity of the ultra-violet absorption band of cod-liver oil at 328 $\mu\mu$; Morton and Heilbron [98]) O. Rosenheim and T. A. Webster [99] state that dehydro-ergosterol shows selective absorption in the ultra-violet region at 320—328 $\mu\mu$. It is inactive in promoting growth and gives no antimony trichloride reaction, from which it is concluded that the spectrographic test, at any rate by itself, cannot be taken as a criterion of vitamin-A.

Amongst those workers who have used the colour test and obtained consistent results are E. R. Norris and I. S. Danielson,[1] E. M. Bailey, H. C. Cannon, and H. K. Fisher,[2] and N. Evers.[3] The first-mentioned and last-mentioned workers stress the importance of the concentration of the oil used in the test. Only at low concentrations

[97] *Biochem. J.*, 1929, **23**, 785; *A.*, 1202.   [98] *Ann. Reports*, 1928, **25**, 268.

[99] *Biochem. J.*, 1929, **23**, 633; *A.*, 1202.

[1] *J. Biol. Chem.*, 1929, **83**, 469; *A.*, 1202.

[2] *Conn. Agric. Exp. Sta. Bull.*, 1928, No. 295, 334; *A.*, 103.

[3] *Quart. J. Pharm.*, 1929, **2**, 227; *A.*, 1203.

is the colour developed proportional to the amount of oil used, and by working at such low concentrations Norris and Danielson obtained results in good agreement with those of the biological method. Bailey, Cannon, and Fisher find a good agreement between the colour test and the standard U.S. Pharmacopœia feeding tests. On the other hand, certain difficulties and inconsistencies in the test were encountered by G. Monasterio,[4] W. S. Jones, A. E. Briod, S. Arzoomanian, and W. G. Christiansen,[5] H. Steudel,[6] H. von Euler, M. Rydbom, and H. Hellström,[7] and by P. B. Hawk.[8] Of these, perhaps the most striking result is that of Euler, Rydbom, and Hellström, who found that the product from an alcoholic extract of a sample of cod-liver oil gave a reaction with about four times the intensity of that of the original oil. Von Euler, Karrer, and Rydbom[9] find that antimony trichloride colour reactions are given by lycopin, bixin, capsanthin, α-crocetin, dihydro-α-crocetin, xanthophyll, di-iodocarotin, dihydro*iso*norbixin, dihydro-α-crocetin methyl ester, fucoxanthin, zeaxanthin, lutein, and tri-iodocarotin. These workers therefore conclude that the test is given by many carotinoids which do not promote growth and hence that the reaction is not generally applicable to the investigation of vitamin-*A*. The depth of colour is very greatly influenced by oxidation of the carotinoid.

Ergosterol and the Formation of Vitamin-D.—Despite many ingenious attacks on the problem, it cannot yet be said that the mechanism of the formation of vitamin-*D* from ergosterol has been elucidated. The course of the various changes which occur when ergosterol is irradiated has been the subject of a spectrographic investigation by R. B. Bourdillon, C. Fischmann, R. G. C. Jenkins, and T. A. Webster.[10] The antirachitic activity of irradiated ergosterol solutions has been compared with their absorption spectra, both before and after removal of unchanged ergosterol, and evidence has been obtained which points to the successive formation of three substances or groups of substances. The first of these shows an absorption band similar to that of ergosterol with a maximum at 280 μμ but more than twice as intense. This substance is believed to be vitamin-*D*. The second product which is formed by further irradiation of the first has a maximum absorption at 240 μμ and has no antirachitic activity. The third substance formed in turn from the second possesses neither antirachitic activity nor specific absorp-

[4] *Biochem. Z.*, 1929, **212**, 66; *A.*, 1343.
[5] *J. Amer. Pharm. Assoc.*, 1929, **18**, 253; *A.*, 610.
[6] *Biochem. Z.*, 1929, **207**, 437; *A.*, 726.
[7] *Ibid.*, 1929, **208**, 73; *A.*, 851.
[8] *Science*, 1929, **69**, 200; *A.*, 1111. [9] *Loc. cit.*
[10] *Proc. Roy. Soc.*, 1929, *B*, **104**, 561; *A.*, 727.

tive capacity. The first substance, which is presumed to be the vitamin, is obtained in the form of colourless glassy masses which have failed to crystallise. Reasons are given for supposing that ergosterol when irradiated changes directly into the vitamin without the loss of any large part of its molecule. Careful measurements of the extinction coefficients during irradiation point to the presence in the purest preparations of the first substance of some 55% of the vitamin. The smallest daily dose of such a preparation which could be detected in the course of a 14-day feeding experiment by radiographic measurements of calcification would be about $1/400,000$ mg., *i.e.*, a total in 14 days of 3.5×10^{-8} g. Multiplied by the above figure of 55%, the result, 1.9×10^{-8} g., represents the amount of the smallest dose of the pure vitamin detectable by these workers' methods. In their own words : " This is in almost ludicrously close agreement with the value (2×10^{-8} g.) found by Fosbinder, Daniells, and Steenbock and by Coward. . . ." [11] An investigation somewhat similar to the foregoing has been carried out by C. E. Bills, E. M. Honeywell, and W. M. Cox,[12] and was referred to in the Report of last year. The results agree with those of Bourdillon and his associates, and also with those of G. Tixier,[13] in not associating the maximum antirachitic activity developed during irradiation with the substance responsible for the absorption band of shorter wave-length (240—253 $\mu\mu$). There is some evidence that a certain degree of antirachitic potency can be developed in ergosterol by irradiation with soft X-rays.[14] The activation is not ascribed to the production of ultra-violet radiations by the X-rays. The change in the absorption spectra of the irradiated product is the same as that produced by ultra-violet irradiation.

Another mode of attack on the problem of the nature of vitamin-D is that of O. Rosenheim and N. K. Adam,[15] who have investigated the unimolecular films formed on water by the irradiation products of ergosterol, and find them to resemble those of certain ketonic cholesterol derivatives. The results are expressed by plotting horizontally the areas per molecule in square Ångstrom units against the lateral compression of the films in dynes per cm., plotted vertically. Ergosterol itself gives the steepest curve, followed by Substance A (vitamin-D), Substance B, Substance C, and oxy-cholestenone with curves of decreasing steepness in the order given. Oxycholesterylene ($\Delta^{4:6}$-cholestadiene-8-one) gives a curve very

[11] *Ann. Reports*, 1928, **25**, 274.   [12] *Ibid.*, p. 273.
[13] *Compt. rend.*, 1929, **188**, 206; *A.*, 359.
[14] A. Knudson and C. N. Moore, *J. Biol. Chem.*, 1929, **81**, 49; *A.*, 359;
R. Delaplace and G. Rebière, *Compt. rend.*, 1929, **188**, 1169; *A.*, 727.
[15] *Proc. Roy. Soc.*, 1929, *B*, **105**, 422.

closely approximating to that of the vitamin and the ultra-violet absorption spectra of the two substances are very closely similar, and of intensity about twice that of ergosterol. Oxycholesterylene is, however, devoid of antirachitic properties both before and after irradiation. The lability of the hydrogen of the secondary alcohol group is considered to be the controlling factor of the changes induced by ultra-violet irradiation of ergosterol, and it is suggested that the vitamin may have to be looked for amongst the ergosterol derivatives formed as by-products in the production of the ketone. Despite its failure to solve the problem of the nature of vitamin-D, the method used by Rosenheim and Adam is one of fascinating ingenuity.

Hypervitaminosis.—It is now recognised that very excessive doses of irradiated ergosterol or other preparations rich in vitamin-D may exercise a very damaging influence on the growing animal. The problem arises purely from the fact that very potent preparations of vitamin-D are available, and is not likely to be encountered in a well-balanced normal diet. Attention was first directed to this problem by Pfannensteil [16] and by H. Kreitmair.[17] L. J. Harris and T. Moore [18] find that young rats lose weight and die on a synthetic diet containing 0·1% of irradiated ergosterol. Some indication was obtained that a considerable increase in the allowance of vitamins-B and -C served to alleviate the condition. It was further shown that the lethal dose of irradiated ergosterol becomes non-toxic concurrently with the destruction of vitamin-D by over-irradiation. In a later paper Harris and Moore [19] show that the manner of irradiation does not influence the severity of the effects and find that excessive doses of ergosterol irradiated in alcohol, in oil, or in the absence of any solvent produce specific ill-effects. L. J. Harris and C. P. Stewart [20] find that a synthetic diet containing 0·1% of irradiated ergosterol produces a marked rise in the inorganic phosphate of the blood and a considerable rise in the serum calcium. The former effect is eventually obtained even in adult animals, although in these the serum calcium does not increase. A general post-mortem finding as a result of " hypervitaminosis " is the widespread occurrence of abnormal deposits of calcium throughout the body, particularly in the vascular system, spleen, kidney, liver, and lungs. J. A. Collazo, P. Rubino, and B. Varela [21] and F. Holtz and T. von Brand [22] have obtained somewhat similar results on admin-

[16] *Klin. Woch.*, 1927, **6**, 2310.
[17] *Münch. med. Woch.*, 1928, **75**, 637; *A.*, 1928, 1406.
[18] *Biochem. J.*, 1928, **22**, 1461; *A.*, 105.
[19] *Ibid.*, 1929, **23**, 261; *A.*, 610.   [20] *Ibid.*, p. 206; *A.*, 610.
[21] *Biochem. Z.*, 1929, **204**, 347; *A.*, 476.
[22] *Z. physiol. Chem.*, 1929, **181**, 227; *A.*, 611.

istering excessive doses of "vigantol," a potent preparation of vitamin-D. The last-mentioned investigators, however, appear to have some doubt concerning the origin of the effect and consider that it may not be due to "hypervitaminosis" but to a toxic impurity in the "vigantol." J. C. Hoyle and H. Buckland,[23] giving 1% ergosterol, irradiated in oil, found no lethal effect for a period of more than 50 days. No persistent or marked loss of weight occurred, but urinary calculi were found post-mortem. It seems probable to the Reporter that considerable variations in the final effect of excessive doses of irradiated ergosterol may be related to the balance of other dietetic factors. Indeed, J. B. Duguid, M. M. Duggan, and J. Gough[24] find that the calcification effects in the muscular and vascular systems described by Kreitmair and Moll are most readily obtained when the irradiated ergosterol is administered along with an otherwise vitamin-free diet although it is possible that factors other than the absence of the other vitamins, *e.g.*, the calcium content of the diet, may be in part responsible for the observed effects.

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A. C. CHIBNALL.
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[23] *Biochem. J.*, 1929, 23, 558; *A.*, 853.   [24] Private communication.

MINERALOGICAL CHEMISTRY.

THE new X-ray methods for the investigation of the structure of crystals have given a great and welcome impetus to the more intensive study of minerals. The numerous workers, who are now attacking the many problems by these methods, may be divided into two schools. Physicists, naturally looking at the matter from a physical point of view, are apt to regard each mineral species as a distinct individual—they speak of " this crystal "; and they are usually content to copy from the text-books data for the molecular weight and density on which to base their calculations, regardless of the fact that these may have been determined by mineralogists on different types of material from separate localities, and different again from the material that is being examined afresh by the X-ray methods. The mineralogist, on the other hand, is apt to treat the empirical formulæ of the text-books with less respect, and, being less familiar with the X-ray data, he has more faith in the results of the physicist. He thus attempts to manipulate the chemical formula to fit the X-ray data, whereas the physicist adjusts the X-ray data to fit the formula. A notable exception to such procedure is mentioned below for tremolite in the amphibole group. To correct the long-accepted and apparently simple formula for a common rock-forming mineral is a great triumph for the new X-ray methods.

Minerals have grown under such varied conditions that we cannot assume two crystals of the same species to be exactly alike, unless perhaps they grew side by side in the same rock cavity. Each crystal has, in fact, its own individuality. It is therefore imperative that the material should be examined not by a single method, but also by other methods, and further, on the same sample of material. For this reason many of the isolated determinations—chemical, physical, or X-ray—now published are practically useless for the purpose of any future correlation of data.

Constitution of Silicates.

The atomic structures of a considerable number of silicate minerals have been worked out in detail by X-ray methods by W. L. Bragg and his co-workers at Manchester. These include beryl, phenakite, olivine, monticellite, the humite group, zircon, topaz, staurolite, kyanite, fibrolite, andalusite, diopside, and tremolite. General collected accounts of this important mass of work have been given

by him.[1] Models have been constructed to represent all these structures, and a series of stereoscopic photographs of these and other models has been issued in conjunction with Sir William Bragg.[2] Two-dimensional pictures of such structures viewed in the usual way often seem to be a mere confused assemblage of balls and rods, but when viewed in the simple folding stereoscope supplied with the photographs they stand out in the solid with remarkable clearness.

A large number of silicates have also been examined by X-ray methods by B. Gossner and his co-workers in Munich. Here, in many cases, the chemical composition and the density have also been determined on the same sample of material. The object of this work has been, not so much to determine the minute structure, but to deduce a chemical formula corresponding with such a molecular weight that a whole number of complete molecules shall be accommodated in the unit cell. The minerals already examined include zunyite, leifite, phenakite and dioptase, nepheline, benitoite, scapolite and melilite groups, apophyllite, cordierite, kornerupine, sapphirine, neptunite, epididymite and eudidymite, thortveitite, rhodonite, babingtonite, and several members of the amphibole group. A brief general account of a portion of this work has been given by Gossner.[3]

With the object of testing the exactness of the stoicheiometric ratios in some common silicate minerals, B. Gossner[4] and his pupils have made careful analyses in duplicate on specially selected material. In four specimens of olivine from different localities the ratio $SiO_2 : RO$ varied from $1 : 1.93$ to $1 : 1.99$, showing a slight excess of silica over that required by the orthosilicate formula; but when the small amount of water (expelled only at $1100°$) is included with the bases the silica shows a slight deficiency, $SiO_2 : RO$ then varying from $1 : 2.00$ to $1 : 2.05$. Three analyses of almandine gave the ratios $R_2O_3 : RO : SiO_2 = 1 : 2.61 : 2.66$, $1 : 2.61 : 2.71$, and $1 : 2.54 : 2.69$, showing in all cases an excess of both alumina and silica over that required by the garnet formula $R_2O_3,3RO,3SiO_2$ or $3SiO_3Fe,Al_2O_3$. The excess of alumina is explained by the isomorphous replacement of Al_2 for $SiFe$ (or Al_2O_3 for $FeSiO_3$) to the extent of 3 mols. %; and the excess of silica over that required for the $RSiO_3$ portion of the formula may perhaps be explained by its filling in odd spaces in the crystal structure, or perhaps by an isomorphous replacement of silica and aluminium, which differ only

[1] *Proc. Roy. Soc.*, 1927, [*A*], **114**, 450; *A.*, 1927, 501; *Proc. Roy. Inst.*, 1927, **25**, 302; *A.*, 1927, 1015; *Trans. Faraday Soc.*, 1929, **25**, 291; *A.*, 749.

[2] First series, 1928; second series, 1929 (Adam Hilger, Ltd., London).

[3] *Ber.*, 1928, **61**, [*B*], 1634; *A.*, 1928, 1172.

[4] *Z. angew. Chem.*, 1929, **42**, 175.

slightly in their atomic radii. An analysis of water-clear sanidine showed, on the other hand, a deficiency in silica, namely 1·077 mols. instead of 1·128 required by the felspar formula.

In certain silicate minerals the small amount of water (1 or 2%), which is expelled only at high temperatures (about 1000°), presents a difficulty in arriving at a satisfactory formula. Such water has often been ignored, being regarded as adsorbed, or present as an adventitious impurity, or due to the incipient decomposition of the mineral. Cases are noted below under amphibole and beryl; and other examples are given by topaz, cordierite, kornerupine, staurolite, etc. It is noted that the X-ray analysis of tremolite now definitely requires the addition of this water in the structure, while apparently in beryl (W. L. Bragg, 1926) the structure can be explained without it. Olivine, always regarded as an anhydrous orthosilicate, also appears to contain some water. B. Gossner [5] has made special tests for water in perfectly fresh olivines from six localities and found 0·78—1·07%; later tests [4] on four more olivines showed 0·79—0·83% of water, which is expelled only at 1100°. M. Aurousseau and H. E. Merwin [6] find only 0·18% of water in olivine from Hawaii.

A recently published book by W. Eitel, " Physikalische Chemie der Silikate " (Leipzig, 1929), deals more especially with the glassy and crystalline conditions of silicates, systems of equilibrium, and the bearing of these on technical problems.

Amphibole Group.—W. Kunitz [7] gives a long series of sixty-one chemical analyses, together with density and optical determinations for various rock-forming members of the amphibole group. The materials were separated by heavy liquids in a centrifugal apparatus from the finely powdered rocks. Seven isomorphous series are distinguished, and these fall into two groups, namely, those (1—4) from crystalline schists and those (5—7) from igneous rocks.

(1) Anthophyllite, $H_2Mg_7Si_8O_{24}$—Grünerite, $H_2Fe_7Si_8O_{24}$.

(2) Tremolite, $H_2Ca_2Mg_5Si_8O_{24}$—Actinolite, $H_2Ca_2Fe_5Si_8O_{24}$.

(3) Glaucophane, $H_2Na_2Mg_3Al_2Si_8O_{24}$—Riebeckite, $H_2Na_2Fe^{II}_3Fe^{III}_2Si_8O_{24}$.

(4) Glaucophane, $H_2Na_2Mg_3Al_2Si_8O_{24}$—Tremolite, $H_2Ca_2Mg_3Mg_2Si_8O_{24}$.

(5) Common green hornblendes (mixtures of syntagmatite and tremolite–actinolite molecules)
$\begin{cases} H_2Ca_2Mg_4Al_2Si_6O_{22}\text{—}H_2Ca_2Fe_4Al_2Si_6O_{22}. \\ H_2Ca_2Mg_5Si_8O_{24}\text{—}H_2Ca_2Fe_5Si_8O_{24}. \end{cases}$

(6) Syntagmatitic hornblendes (including pargasite and basaltic hornblende) $H_2Ca_2Mg_4Al_2Si_6O_{22}\text{—}H_2Ca_2Fe_4Al_2Si_6O_{22}.$

(7) Alkali–iron–amphiboles (imerinite, hastingsite, katophorite, arfvedsonite) $H_2Na_2Mg_4Si_8O_{22}\text{—}H_2Na_2Fe_4Si_8O_{22}.$

[5] *Centr. Min.*, 1926, [*A*], 307.

[6] *Amer. Min.*, 1928, **13**, 559.

[7] *Jahrb. Min., Beil.-Bd.*, 1929, [*A*], **60**, 171.

In several of these series the density and refractive indices show a regular increase with increasing iron content. In the basaltic hornblendes the refractive indices also increase with the percentage of titanium dioxide. The formulæ written in the following manner :

Anthophyllite .... $[(SiO_3)_8]H_2Mg_2Mg_2Mg_3$
Tremolite .... $[(SiO_3)_8]H_2Ca_2Mg_2Mg_3$
Glaucophane .... $[(SiO_3)_8]H_2Na_2Al_2Mg_3$
Syntagmatite .... $[(SiO_3)_6(AlO_2)_2]H_2Ca_2Mg_2Mg_2$
Arfvedsonite .... $[(SiO_3)_6(SiO_2)_2]H_2Na_2Mg_2Mg_2$

show more clearly the replacements of [NaAl] for [CaMg], of [NaSi] for [CaAl], etc. These isomorphous replacements are discussed in connexion with the sizes of atoms, and whether hornblende, augite, or mica should separate from the magma under various conditions.

B. Gossner [8] with F. Mussgnug and F. Spielberger have examined various members of the amphibole group, chemically and by X-ray methods, with the idea of adjusting the formulæ so that a whole number of complete molecules shall be contained in the unit cell. By the rotating-crystal method they obtain the following dimensions for the unit cell :

	a.	b.	c.	Axial angle β.
Actinolite	9·91 Å	18·5 Å	5·36 Å.	74° 24′
Glaucophane	9·72	17·89	5·37	74 50
Basaltic hornblende	9·88	18·10	5·31	74 15
Arfvedsonite	9·87	18·31	5·33	,,
Barkevikite	9·92	18·30	5·33	,,
Kaersutite	9·85	18·17	5·39	,,
Aenigmatite	10·02	14·73	5·12	101 58, a and γ about 90°.

All these, with the exception of aenigmatite, show a close agreement, and they can be referred to the general formula (" Bauplan," or building scheme) $Si_2O_6Mg_2,Si_2O_6MgCa$ [i.e., the tremolite formula $CaMg_3(SiO_3)_4$], with four molecules in the unit cell, or eight molecules of the type $R_2Si_2O_6$. Individual analyses are explained by the isomorphous mixing of a great variety of molecules derived by replacement from these two part molecules. For example, Si_2O_6MgCa may be replaced by $Si_2O_6Mg_2$, $Si_2O_6Na_2H_2$, $Si_2O_6Na_4$, Si_2O_6AlNa, and finally by $Al_2O_6Na_2H_2$; whilst $Si_2O_6Mg_2$ changes with TiO_6Fe_2, Al_4O_6, or Fe_4O_6. In an actual case, the arfvedsonite analysed is represented by the following molecules :

0·190 $Si_2O_6Fe_2$	0·066 Si_2O_6FeCa
0·003 Fe_4O_6	0·050 $Si_2O_6Fe(NaH)$
0·007 Al_4O_6	0·011 $Si_2O_6Mn(NaH)$
———	0·053 $Si_2O_6(NaH)_2$
0·200	0·020 $Si_2O_6Na_4$
	———
	0·200

[8] *Jahrb. Min., Beil.-Bd.*, 1928, [A], **58,** 213; *Centr. Min.*, 1929, [A], 5; *Z. Krist.*, 1929, **72,** 111; *A.*, 1223.

Aenigmatite and cossyrite present a difficulty, and various orientations of the crystals and alternative formulæ are tested. With the cell dimensions quoted above, the general formula that appears the most probable is $6SiO_3Fe,TiO_3Fe$, allowing for two molecules in the unit cell, or seven molecules of the general type $R_2Si_2O_6$. Aenigmatite therefore does not strictly fall into the amphibole group. Similarly, rhodonite,[9] babingtonite,[10] and wollastonite do not conform with the monoclinic pyroxenes, which contain four molecules of $R_2Si_2O_6$ in the unit cell, nor with the orthorhombic pyroxenes with eight molecules of $R_2Si_2O_6$.

F. Machatschki[11] deduces a general formula for the monoclinic amphiboles as $XY_3(Si,Al)_4(O,OH,F)_{12}$, where $X = Ca$, Na, K, and $Y = Mg$, Fe^{II}, Fe^{III}, Al, also Ti and Mn. The special case discussed is based on the chemical analysis of a hypersthene–hornblende rock from Greenland, and after deducting 16% of hypersthene and neglecting small amounts of olivine and iron ores, the special formula deduced for this hornblende is

$$(Ca_3Na)(Mg_9Fe^{II}_2Fe^{III})(Al_3Si_{13})(O_{45}[OH]_3).$$
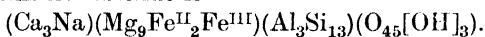
The mutual replacement of atoms in the " X " and " Y " groups and of Al for Si depends, not on their valencies, but on their sizes being such that they will fit into the crystal structure, with a certain accommodation between different pairs, for example, Al for Si together with OH for O. The assumption of the replacement of aluminium for silicon is made to account for the occasional deficiency in silica below the metasilicate ratio; but it seems curious to think of aluminium taking the part of silicon in a silicate. Any variation shown by analyses from the ratio $X : Y = 1 : 3$ is further explained by an interchange of atoms between these two groups. Obviously by shuffling atoms about in this way any analysis might be fitted in with any formula.

B. E. Warren[12] has determined for tremolite from New York the cell dimensions $a = 9.78$, $b = 17.8$, $c = 5.26$ Å. ($a : b : c = 0.550 : 1 : 0.295$, $\beta = 73° 58'$), with two molecules $H_2Ca_2Mg_5(SiO_3)_8$ in the unit cell. Except for the double length of the b-axis, these dimensions are very close to those of diopside,[13] and with certain modifications, the arrangement of the atoms is very similar in the two minerals. Tetrahedral groups of four oxygen atoms surrounding each silicon atom are linked by shared oxygens to form endless chains parallel to the vertical c-axis of the crystal. In tremolite

[9] B. Gossner and K. Brückl, *Centr. Min.*, 1928, [A], 316; *A.*, 495.

[10] B. Gossner and F. Mussgnug, *ibid.*, 1928, [A], 274; *A.*, 382.

[11] *Z. Krist.*, 1929, **71**, 219.

[12] *Ibid.*, **72**, 42; *Abs. Theses Mass. Inst. Tech.*, 1929, No. 4, 74; *A.*, 1130.

[13] B. E. Warren and W. L. Bragg, *Z. Krist.*, 1928, **69**, 168; *A.*, 1223.

two such diopside chains are linked together and there are four chains in the unit cell. The calcium and magnesium atoms, all lying on diad axes, are surrounded by eight and six oxygens respectively. Such a structure will accommodate only ten magnesium atoms in the unit cell, and the two extra ones required by the usually-accepted formula $CaMg_3(SiO_3)_4$ are replaced by four (OH) groups, which occupy the same space as four oxygen atoms. The new formula, requiring $2 \cdot 2\%$ of H_2O, agrees well with the best published analyses when these are recalculated with small isomorphous replacements (Si,Al), (Mg,Fe), (Ca,Na,K), and (OH,F); but the presence of water was not actually proved in the sample of material used for the X-ray analysis. This crystal structure explains the fibrous texture of the mineral, which is very prominent in the amphibole-asbestos variety, and the prism-cleavage of 56°.

This new formula, $H_2Ca_2Mg_5(SiO_3)_8$, for tremolite, deduced from a consideration of the crystal structure as determined by X-ray methods, is identical with that arrived at independently and by quite another method by W. Kunitz (see above), and it seems to be fully established. The apparently simple formula $CaMg_3(SiO_3)_4$ for this common rock-forming mineral has been familiar in the text-books since the third edition (1850) of Dana's " System of Mineralogy." P. A. von Bonsdorff in 1821 found about 1% of fluorine and water in tremolite; Penfield and Stanley (1907) found $2 \cdot 03\%$; Allen and Clement (1908) $2 \cdot 31—3 \cdot 04\%$; and W. Kunitz (1929) $1 \cdot 97—2 \cdot 28\%$ in actinolite. This water is expelled only at temperatures up to 1000°. Penfield and Stanley accounted for it, partly in a bivalent group $R^{III}O(F,OH)_2$, and partly as acid hydrogen in their general formula $H_8Si_4O_{12}$ for the " amphibole acid," which was supposed to have a controlling influence (" mass effect ") on the isomorphous replacements. Allen and Clement regarded the water as " dissolved " in the crystal and not chemically combined. The new formula appears to have been first given by P. Niggli in the second edition of his " Lehrbuch der Mineralogie " (1926, vol. 2, p. 468), where, after quoting the usual formula, he remarks that part of the magnesium is almost always replaced by hydrogen and that many analyses agree well with the formula $[SiO_4,SiO_2]_4Ca_2Mg_5H_2$. In a rather more obscured form it was earlier given by B. Gossner[14] as $[2SiO_3Ca,4SiO_3Mg],[2SiO_2,MgO_2H_2]$, which reduces to $H_2Ca_2Mg_5Si_8O_{24}$.*

S. Kôzu[15] has found that when common hornblende is heated to

[14] Z. Krist., 1924, 60, 364.

[15] S. Kôzu, B. Yoshiki, and K. Kani, Sci. Rep. Tôhoku Imp. Univ., 1927, [3], 3, 143.

* Note added in proof.—The formula $8SiO_2,5MgO,2CaO,H_2O$ was suggested by W. T. Schaller, Bull. U.S. Geol. Survey, 1916, 610, 136; A., 1916, ii, 631.

750° there is a marked contraction in volume and a sudden change in the optical constants, the material being then changed into the high-temperature modification corresponding with basaltic hornblende. This change appears to be of some structural significance.

Apophyllite.—New analyses of apophyllite from various localities by B. Gossner and O. Kraus [16] show that small amounts of fluorine are invariably present. A new formula is written in the form $4[H_2Si_2O_5,Ca(OH)_2],KF$, in which part of the fluorine is replaced by hydroxyl and a small amount of potassium by sodium. The water commences to be lost only at 245° with a destruction of the crystal structure, and it does not behave like water of crystallisation or zeolitic water. X-Ray examination gives a unit tetragonal cell of dimensions $a = 12·73$, $c = 15·84$ Å., containing four molecules. The pronounced optical anomalies are explained by the partial replacement of fluorine by hydroxyl, the difference in volume of these constituents causing a strain in the crystal structure.

Andalusite, Fibrolite, and Kyanite.—These trimorphous aluminium silicates, though very different in their physical characters, are found by X-ray analysis to have much the same size of unit cell, containing in each case four molecules Al_2SiO_5. In the following table of the cell dimensions those of topaz are added for comparison.

	a.	*b.*	*c.*	Space-group.
Andalusite [17]	7·76 Å.	7·90 Å.	5·56 Å.	V_h^{12}
Fibrolite [18]	7·43	7·58	5·74	V_h^{16}
Kyanite [19]	7·09	7·72	5·56	?
,, [20]	7·122	7·883	5·650	?
Topaz [21]	4·64	8·78	8·38	V_h^{16}

These minerals, which with the exception of kyanite are all orthorhombic, show several curious relations that have not yet been elucidated. Andalusite has a certain crystallographic relation to topaz; and the manganiferous variety " viridine " has on optical grounds been regarded as a distinct species. Fibrolite also has a peculiar satellite " mullite," the structure of which cannot be distinguished from that of fibrolite. The chemical formula $Al_6Si_2O_{13}$

[16] *Z. Krist.*, 1928, **68**, 595; *A.*, 1036.

[17] W. H. Taylor, *ibid.*, 1929, **71**, 205.

[18] *Idem, ibid.*, 1928, **68**, 503.

[19] W. L. Bragg and J. West, *Proc. Roy. Soc.*, 1927, [*A*], **114**, 450; *A.*, 1927, 501; W. H. Taylor and W. W. Jackson, *ibid.*, 1928, [*A*], **119**, 132; *A.*, 1928, 693; S. Náray-Szabó, W. H. Taylor, and W. W. Jackson, *Z. Krist.*, 1929, **71**, 117.

[20] C. M. Cardoso, *Fortschr. Min. Krist. Petr.*, 1927, **12**, 18; *Ber. Sächs. Akad. Wiss.*, 1928, **80**, 165; E. Schiebold and C. M. Cardoso, *Fortschr. Min. Krist. Petr.*, 1929, **13**, 61.

[21] N. A. Alston and J. West, *Proc. Roy. Soc.*, 1928, [*A*], **121**, 358; *Z. Krist.*, 1928, **68**, 149; *A.*, 15.

assigned to " mullite " is explained as perhaps due to the partial replacement of silicon atoms by aluminium atoms in the fibrolite structure.[18]   In the triclinic kyanite the angles between the crystallographic axes and the edges of the unit cell are $\alpha = 90° 5\frac{1}{2}'$, $\beta = 101° 2'$, $\gamma = 105° 44\frac{1}{2}'$; but other axes can be chosen, all approximately at right angles, namely, $\alpha = 90° 5\frac{1}{2}'$, $\beta = 90° 5'$, $\gamma = 90° 27'$, the dimensions of this pseudo-rhombic cell being $a' = 26·868$, $b' = 7·883$, $c' = 5·650$ Å.   This corresponds with a slightly distorted close-packed cubic structure marked out by the oxygen atoms.   Oxygen atoms are grouped tetrahedrally around the silicon atoms, and octahedrally around the aluminium atoms, as in topaz (p. 265) and staurolite (p. 265).

Beryl.—A set of detailed analyses [22] made on beryls of different types shows considerable deviations from the usually accepted formula $Be_3Al_2Si_6O_{18}$.   The pink tabular crystals of the " rosterite " variety from Elba contain appreciable amounts of alkalis (Li_2O 0·43, Na_2O 4·22, K_2O 2·25, Cs_2O 0·91%) together with water 0·84%. " Emerald " from Colombia gave less alkalis (0·88%), but more water (1·84%), together with Cr_2O_3 0·077%, accounting for the colour; and clear blue " aquamarine " from Siberia gave alkalis 1·04%, water 0·98%.   The variations in composition are explained by assuming mixtures with the main molecule $Be_3Al_2Si_6O_{18}$ of molecules R_2SiO_3 and $R_2Al_2Si_2O_8$, where R_2 is Li_2, Na_2, K_2, Cs_2, together with some Be, Ca, Mg.   Small amounts of alkalis and water have also been found in beryl from Japan.[23]

Certain transparent green beryls when heated to 400—450° change in colour to blue;[24] and this is now much used in the trade for improving the colour of these gem stones.

Epididymite and Eudidymite.—These rare dimorphous minerals with the composition $HNaBeSi_3O_8$ are found by X-ray methods to have unit cells of very nearly the same dimensions :

	a.	*b.*	*c.*	Mol. vol.	Space-group.
Epididymite [25] ...	12·65 Å	7·41 Å	13·53 Å.	158·5	V_h^{17}
Eudidymite [26] ...	12·70	7·34	14·01	159·3	C_{2h}^6

In each case the unit cell contains eight molecules and the arrangement of the atoms is probably much the same.   There is, however, a wide difference in the axial angle, epididymite being orthorhombic

[22] F. Zambonini and V. Caglioti, *Gazzetta*, 1928, **58**, 131; *A.*, 1928, 731.

[23] T. Uemura, *Japan. J. Chem.*, 1926, **2**, 117; *A.*, 1928, 1211; J. Yoshimura, *Bull. Chem. Soc. Japan*, 1926, **1**, 239; *A.*, 1927, 129.

[24] J. Kurbatov and W. Kargin, *Centr. Min.*, 1927, [*A*], 361; *A.*, 1928, 730.

[25] B. Gossner and F. Mussgnug, *Festschr. V. Goldschmidt*, Heidelberg, 1928, 117.

[26] B. Gossner and O. Kraus, *Centr. Min.*, 1929, [*A*], 257.

($\beta = 90°$) and eudidymite monoclinic with $\beta = 77° 26'$. This low degree of polymorphism is somewhat similar to that of α- and β-quartz.

Felspar Group.—F. Machatschki [27] points out that W. Wahl's co-ordination formulæ (*Ann. Reports*, 1927, **24**, 294) for albite $[Al_2(SiO_3)_2(Si_2O_5)_2]Na_2$ and anorthite $[Al_2O_2(SiO_3)_2]Ca$ do not explain the isomorphism of this pair of minerals in the series of plagioclase felspars. As the fundamental unit of silicate structures, he takes a tetrahedral group of four O^{-2} ions around a Si^{+4} ion. Aluminium Al^{+3} with O^{-2} may have a co-ordination number 4 or 6, and when 4 it may take the place of silicon in the tetrahedral group of oxygens. Similarly, Be^{+2} and perhaps B^{+3} may also occupy this position. Since tetrahedra cannot fill space, the cavities between them may be occupied by the metal ions. In the felspar type of silicate structure (where $Si + Al : O = 1 : 2$) every oxygen ion is common to two adjacent tetrahedra, and the " formulæ " are written

Albite ...
$$\begin{bmatrix} (SiO_2)_3 \\ AlO_2 \end{bmatrix}^{-1} Na^{+1}.$$
Anorthite ...
$$\begin{bmatrix} (SiO_2)_2 \\ (AlO_2)_2 \end{bmatrix}^{-2} Ca^{+2}.$$
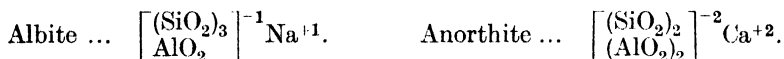
Formulæ on similar lines are also suggested by Machatschki for the metasilicates and the orthosilicates. In his " metatype," with SiO_3 or AlO_3, two oxygen ions are in common for adjacent tetrahedra, and an endless chain (similar to that deduced by B. E. Warren and W. L. Bragg for the pyroxenes and amphiboles, p. 257) is represented by

" Metatype " ...
$$\begin{bmatrix} O & O & O & O \\ | & | & | & | \\ -Si-O-Si-O-Si-O-Si-O \\ | & | & | & | \\ O & O & O & O \end{bmatrix}^{-8} R^{II}_4 (or\ R^{I}_2 R^{III}_2).$$
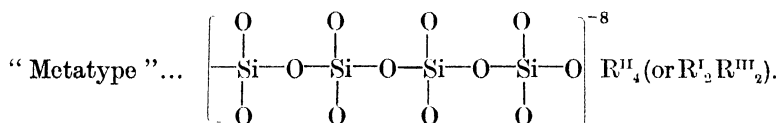
In his " orthotype " there is no linking of oxygen ions in adjacent tetrahedra, and here separate molecules can exist, the formula being then of the ordinary co-ordination kind.

" Orthotype " ....
$$\begin{bmatrix} O \\ O \end{bmatrix} Si \begin{matrix} O \\ O \end{matrix}^{-4} R^{II}_2\ (or\ R^{I}R^{III}).$$
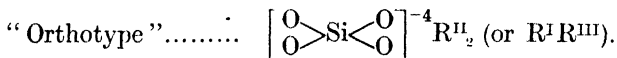
In the " felspar type " and the " metatype " the structures are continuous and there are no separate molecules. These are the " open structures " of W. L. Bragg and J. West,[28] which include quartz, beryl, phenakite, etc. For beryl, the metatype formula is written as $[(SiO_2)_6(BeO_2)_3]^{-6} Al^{+3}Al^{+3}$.

The unit cell dimensions of the various felspars, as determined by

[27] *Centr. Min.*, 1928, [*A*], 97; *A.*, 1928, 1349.
[28] *Proc. Roy. Soc.*, 1927, [*A*], **114**, 469; *A.*, 1927, 501.

E. Schiebold,[29] are tabulated below. The base-centred cell contains four molecules $KAlSi_3O_8$ (orthoclase), $NaAlSi_3O_8$ (albite), or $CaAl_2Si_2O_8$ (anorthite). In the plagioclase felspars, the substitution of Na–Si for Ca–Al in passing from albite to anorthite is accompanied by a small contraction of the lattice, the greatest variation being in the c-axis. The change of the molecular volume is, however, not an exact linear function of the chemical composition, there being a maximum at the albite–anorthite mixture 1 : 1, corresponding with labradorite. The entry of potassium causes a considerable enlargement of the lattice dimensions, the a-axis showing the greatest change whilst the c-axis is here little affected. The X-ray examination emphasises the pseudo-cubic character of the felspars, and the structure can be considered as based on a close-packed arrangement of 32 oxygen atoms.

	a.	b.	c.	a.		β.		γ.	
Adularia	8·61Å.	13·07Å.	7·26Å.	90°	0′	116°	3′	90°	0′
Sanidine	8·42	12·92	7·14	90	0	115	35	90	0
Microcline	8·44	13·00	7·21	90	7	115	50	89	55
Hyalophane...	8·50	12·92	7·12	90	0	115	35	90	0
Albite	8·23	13·00	7·25	94	3	116	29	88	9
Oligoclase ...	8·16	12·90	7·13	93	4	116	22	90	4
Labradorite...	8·23	12·91	7·16	93	31	116	3	89	57
Anorthite ...	8·185	12·895	7·09	93	13	116	55	91	12

The felspars have been studied from many points of view. They are important constituents of most kinds of igneous rocks, and the classification of such rocks is in part based on the kind of felspar that they contain. Ready means for the determination of the felspars are therefore needed. Graphs plotting the variation of the various optical data with the chemical composition are given in the text-books on petrography and rock-forming minerals. The several graphs of refractive indices and chemical composition have been examined critically by H. L. Alling,[30] and collecting together the data on which these have been based, he finds that in many cases they depend on old and untrustworthy chemical analyses, and that the optical data have not always been determined on the material actually analysed. Much attention has been paid to the determination of the felspars by the Fedorov method with the aid of the universal microscope stage. The felspar in a thin rock-slice is covered with a glass hemisphere of nearly the same refractive index as that of the mean of the mineral, and it can be brought into any desired position by rotation about three axes at right angles, these axes being provided with graduated circles. By this means the

[29] *Fortschr. Min. Krist. Petr.*, 1927, **12,** 78; 1929, **14,** 62; *Trans. Faraday Soc.*, 1929, **25,** 315; *A.*,749.
[30] *J. Geol.*, 1929, **37,** 462.

different types of twinning, the orientation of the three principal directions of vibration, and the optic axial angle can be determined and plotted on graphs. This method has been largely developed by L. Duparc and his pupils in Geneva, and a summary of recent work is given in " Mineralogical Abstracts." [31]

The felspar diagram orthoclase–albite–anorthite has been studied in detail by J. H. L. Vogt.[32] Various equilibrium diagrams are given, and he tabulates the Or : Ab : An ratios in the rock, in the separated felspars, and in the residual magma. Finally, the felspars have been studied from the point of view of their application in ceramics, enamel-ware, etc.[33]

Melilite Group.—The following X-ray data have been determined by B. Gossner and ·F. Mussgnug : [34]

	Mols. in unit cell.	a.	c.
Gehlenite ...	4 Mols. SiO_4Ca_2,Al_2O_3	11·11 Å	5·06 Å.
Melilite	4 Mols. CaO,Si_2O_6CaMg	11·12	5·09
Sarcolite	6 Mols. $Si_3O_8AlNa,Si_2O_8Al_2Ca,3CaO$	17·6	15·59

Gehlenite and melilite, both with the space-group D_{4h}^3, are thus closely related, and their composition is expressed as mixtures of the molecules CaO,SiO_3Ca,Al_2O_3 (velardeñite), CaO,SiO_3Ca,SiO_3Mg (åkermanite), and CaO,SiO_3NaSiO_3Al, in which there may also be replacements $Al_2 = SiMg$, $CaMg = NaAl$, and $SiNa = AlCa$. On the other hand, sarcolite, with space-group C_{4h}^5, is more closely related to the scapolite group, and the composition is expressed as an addition compound of scapolite ($3Si_2O_8Al_2Ca,CaO$) with $3\frac{1}{2}CaO$.

From a consideration of the published analyses of the minerals åkermanite, humboldtilite, melilite, gehlenite, and sarcolite, H. Berman[35] deduces a general formula for the whole group as $(Ca + Na)_{20-x}Mg_yAl_zSi_{30-(y+z)}O_{70}$, where $x = 0$ to 3, $y = 0$ to 10, and $z = 0$ to 20. End members of the series are : åkermanite, $Ca_2MgSi_2O_7$; gehlenite, $Ca_2Al_2SiO_7$; soda-melilite, $Na_2Si_3O_7$; and sub-melilite, $CaSi_3O_7$.

Mica Group.—J. Jakob [36] has continued his work of laboriously analysing a large number of micas, giving also in some cases optical data for the material analysed, but no density determinations. Since the last Report he has made 28 new analyses of muscovites and

[31] *Min. Mag.*, 1928, Abstr., **3**, 515.
[32] *Skrifter Norske Vidensk. Akad.*, 1926, No. 4.
[33] *B.*, 1928, 53, 193, 263.
[34] *Centr. Min.*, 1928, [*A*], 129, 167.
[35] *Amer. Min.*, 1929, **14**, 389.
[36] *Z. Krist.*, 1928, **69**, 217; 1929, **69**, 403, 511; 1929, **70**, 493; 1929, **72**, 327; *A.*, 1263.

phlogopites. For individual specimens such formulæ as the following are deduced for muscovite and phlogopite respectively :

$$29 \cdot 98 \left[Al(SiO_6SiO_2)_3 \right]_{\substack{Al_5 \\ K_{3 \cdot 198} \\ H_{2 \cdot 803}}} + 25 \cdot 19 \left[Al(SiO_4SiO_2)_3 \right]_{\substack{Al_3 \\ K_{1 \cdot 599} \\ H_{1 \cdot 491}}} + 44 \cdot 83 \left[Al(SiO_6SiO_2)_3 \right]_{\substack{Al_5 \\ K_{1 \cdot 599} \\ H_{4 \cdot 191} \\ Mg_{1 \cdot 650}}}$$

$$59 \cdot 97 \left[Al(SiO_4)_3 \right]_{\substack{Al_3 \\ K_{1 \cdot 993} \\ H_{1 \cdot 007}}} + 20 \cdot 17 \left[Mg(SiO_5)_5 \right]_{\substack{Mg_{7 \cdot 566} \\ H_{0 \cdot 868}}} + 19 \cdot 86 \left[Mg(SiO_5)_5 \right]_{\substack{Mg_{7 \cdot 566} \\ H_{5 \cdot 868}}}$$
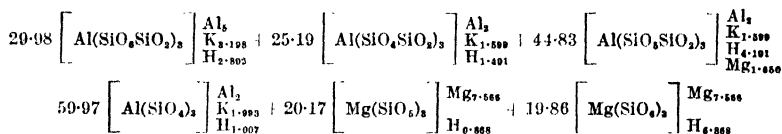
W. Kunitz [37], seeing that some of his analyses do not check with those of Jakob made on material from the same locality, has repeated his work and finds that calcium enters only occasionally in very small amounts into the composition of muscovite and biotite.

The composition of the micas has been further discussed by A. N. Winchell [38] and A. F. Hallimond,[39] the debatable points being whether the ratio $K_2O : SiO_2$ is constant or not at 1 : 6, and whether Al_2O_3 replaces RO or $MgSiO_3$.

X-Ray examinations of the micas have so far led to no definite results. The superposed lamellæ show rotations and oblique translations and the data obtained do not appear to give the true crystal lattice.[40]

Nepheline.—J. Morozewicz [41] reviews recent work on the composition of nepheline and adheres to the formula he proposed in 1907, namely $K_2Al_2Si_3O_{10}, nNa_2Al_2Si_2O_8$, where n is usually 4 but may vary to 6. This is regarded as a double salt rather than an isomorphous replacement of potassium and sodium. Four new analyses of elæolite are in agreement with this formula. The rocks from which the analysed mineral was separated show a range of silica from 54·95 to 62·86%, and the $K_2O : Na_2O$ ratio ranges from 1 : 2·3 to 1 : 23·6. In spite of this variation in composition of the magma from which the mineral crystallised, the $K_2O : Na_2O$ ratio in the mineral varies only from 1 : 4 to 1 : 4·5.

X-Ray examination of water-clear nepheline from Vesuvius by B. Gossner [42] gave a unit hexagonal cell of dimensions $a = 10 \cdot 05$, $c = 8 \cdot 43$ Å., and containing twelve molecules $Na_2Al_2Si_2O_8$. Etch-figures suggest that nepheline belongs to the hexagonal-pyramidal class, whilst the other physical characters suggest the dihexagonal-bipyramidal class. The X-ray data point to the latter with the

[37] *Z. Krist.*, 1929, **70**, 508.

[38] *Amer. Min.*, 1927, **12**, 267; 1928, **13**, 52, 567.

[39] *Ibid.*, 1927, **12**, 413; 1928, **13**, 451.

[40] C. Mauguin, *Compt. rend.*, 1928, **186**, 879; *A.*, 1928, 463; C. Mauguin and L. Graber, *ibid.*, 1928, **186**, 1131; *A.*, 1928, 611; C. Mauguin, *ibid.*, 1928, **187**, 303; *A.*, 1928, 1077; C. Mauguin, *Bull. Soc. franç. Min.*, 1928, **51**, 285.

[41] *Bull. Acad. Polonaise*, 1928, [*A*], 111; *A.*, 45.

[42] *Centr. Min.*, 1927, [*A*], 150.

space-group C_{6v}^2. C. Gottfried [43] finds a unit hexagonal cell $a =$ 10·09, $c = 8·49$ Å. containing twenty-four molecules $NaAlSiO_4$, and space-group C_6^6.

Staurolite.—The following X-ray determinations by different authors show a close agreement in the dimensions of the unit cell, but there are considerable differences in the chemical formula. No new analyses or density determinations have been made of the material examined.

Mols. in unit cell.	a.	b.	c.	Space-groups.
(1) [44] 2 Mols. $HFe_2Al_9Si_4O_{24}$	7·84 Å	16·52 Å	5·61 Å.	V_h^{11}
(2) [45] 4 Mols. $HFeAl_5Si_2O_{13}$	7·81	16·59	5·64	V_h^{17}
(3) [46] 4 Mols. $H_2FeAl_4Si_2O_{12}$	7·82	16·52	5·63	V_h^{17}

Selecting fresh axes and another unit cell for kyanite, Cardoso [45] traces a relation between kyanite and staurolite for the purpose of explaining the regular intergrowth of these two minerals. Náray-Szabó [46] also suggests a relation between the structures of kyanite and staurolite, and supposes the staurolite structure to be represented by alternate slabs of $Fe(OH)_2$ and $2Al_2SiO_5$ (kyanite).

Topaz.—A unit cell of dimensions $a = 4·64$, $b = 8·78$, $c = 8·37$ Å. and containing four molecules $[Al(F,OH)]_2SiO_4$ was deduced by J. Leonhardt in 1923 for topaz from San Luis Potosi, Mexico. L. Pauling,[47] using the co-ordination theory of ionic crystals, assumed the fundamental polyhedra for topaz to be an octahedron of oxygen and fluorine anions surrounding each aluminium ion, and a tetrahedron of oxygen ions about each silicon ion. The structure so deduced agrees with the data of Leonhardt. This has been confirmed by N. A. Alston and J. West,[48] who find for topaz from Nigeria the unit cell dimensions $a = 4·64$, $b = 8·78$, $c = 8·38$ Å. The close agreement in these figures for material from different localities is remarkable when we consider that topaz may range in chemical composition from fluor-topaz $(AlF)_2SiO_4$ to hydroxy-topaz $(AlOH)_2SiO_4$ and in density from 3·35 to 3·65. Colourless to faint bluish or greenish crystals are abundant in the alluvial tin deposits of Northern Nigeria; but this material has never been analysed chemically. From determinations of the refractive indices ($\alpha = $ 1·615—1·621, $\beta = 1·622$—1·628) and optic axial angle ($2V = 64° 28'$— $65° 54'$), A. Schoep [49] concludes that these crystals are fluor-topaz containing about 20% of fluorine.

[43] *Z. Krist.*, 1927, **65,** 100.   [44] C. Gottfried, *ibid.*, **66,** 103.
[45] Refs. as (20).   [46] S. Náray-Szabó, *Z. Krist.*, 1929, **71,** 103.
[47] *Proc. Nat. Acad. Sci.*, 1928, **14,** 603; *A.*, 1928, 1176.
[48] *Proc. Roy. Soc.*, 1928, [*A*], **121,** 358; *A.*, 15; *Z. Krist.*, 1928, **69,** 149.
[49] *Natuurwetensch. Tijds.*, 1928, **10,** 3; *A.*, 1928, 503.

Tourmaline.—W. Kunitz [50] gives twenty new chemical analyses, together with density and refractive index determinations, for tourmalines from various localities. He divides them into two series : the dravite series of magnesium–iron tourmalines, and the rubellite series of lithium–iron tourmalines; and the chemical composition is explained by the isomorphous mixing of the following molecules :

(1) Dravite molecule	....	$H_xNa_2Mg_6Al_{12}Si_{12}B_6O_{62}$
(2) Schorl ,,	....	$H_8Na_2Fe_6Al_{12}Si_{12}B_6O_{62}$
(3) Rubellite ,,	....	$H_8Na_2[LiAl]_3Al_{12}Si_{12}B_6O_{62}$
(4) " Uvite " ,,	....	$H_8Ca_2Mg_8Al_{10}Si_{12}B_6O_{62}$
(5) "Tsilaisite" molecule	....	$H_8Na_2Mn_6Al_{12}Si_{12}B_6O_{62}$
(6) (Higher alumina)	....	$H_8Na_2Fe_5Al_{14}Si_{11}B_6O_{62}$

In most cases the composition can be explained by a mixture of two of these molecules : (1) and (2) for the dravite series, and (2) and (3) for the rubellite series. In both these series the density and refractive indices show a regular increase with the increase of the schorl or iron molecule. In the dravite series the vertical crystallographic axis c shows a slight decrease with increasing iron content. The extra molecules (4), (5), and (6) are invoked to explain the composition of tourmalines richer in calcium (up to 5·35% CaO), manganese (up to 8·21% MnO), and aluminium. The lithium in the rubellite molecule is quite distinct from the other alkali metals, and it forms a group [LiAl] replacing [MgMg], similar to the replacement of [LiAl] for [CaMg] in the pyroxenes and of [Li_2Si] for [Fe^{II}]$_3$ in the lithia micas. These replaceable groups have the same sum of the valencies and nearly the same sum of atomic volumes. The above formulæ are intended to express the close relationship between the tourmalines and the micas.[51] These minerals occur in intimate association in rocks, and tourmaline is often found altered to mica.

F. Machatschki [52] from a collection of published analyses deduces, on the same lines as he did for the monoclinic amphiboles and pyroxenes (p. 257), a general formula for tourmaline as $XY_9B_3Si_6H_xO_{31}$, where X = Ca, Na, and some Mn^{II}, and Y = Li, Mg, Mn, Fe, Al. Special formulæ to fit particular analyses range from $Ca_3(Mg_{10}Al_{17})B_9Si_{18}H_{10}O_{93}$ to $Na_3(LiAl_{26})B_9Si_{18}H_5O_{93}$. From X-ray rotation photographs he gets for different tourmalines dimensions ranging from $a = 15·81$, $c = 7·10$ Å. to $a = 16·02$, $c = 7·22$ Å. for the unit hexagonal cell containing three molecules $XY_9B_3Si_6H_xO_{31}$, but the number of atoms is too complex for any attempt at their grouping.

[50] *Chem. Erde,* 1929, **4**, 208; *A.,* 905.

[51] W. Kunitz, *Fortschr. Min. Krist. Petr.,* 1927, **11**, 313; *A.,* 1928, 148.

[52] *Z. Krist.,* 1929, **70**, 211.

Miscellaneous Minerals.

Boleite and Cumengeite.—Preliminary results [53] of an X-ray examination of boleite gave a cubic unit cell of edge 15·6 Å. containing thirty-two molecules $PbCl_2,Cu(OH)_2$. A new analysis of cubo-octahedral crystals has given the formula

$$3PbCl_2,3Cu(OH)_2,AgCl,$$
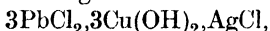
and further X-ray examination shows a unit cube of edge 15·40 Å. containing nine such molecules.[54] Cumengeite [54] occurs as tetragonal pyramids on the six faces of cubes of boleite. Analysis gave the formula $4PbCl_2,4Cu(OH)_2,H_2O$, and the cell dimensions are $a = 15·17$, $c = 24·71$ Å. Calculation gives eleven such molecules in the unit cell, but this number does not agree with the body-centred structure of space-group D_{4h}^{17}. To fit the X-ray data there must be forty-four molecules $PbCl_2,Cu(OH)_2$ in the unit cell. The closeness of the a dimensions of boleite and cumengeite allows of the parallel growth of these two minerals. The cubo-octahedral crystals of boleite show only slight optical anomalies, and the so-called " cubic boleite " or pseudo-boleite occurring as simple cubes is distinguished by a higher double refraction in its outer zones. Analysis and the X-ray patterns show that these are really identical, the surface differences being evidently due to an intergrowth with cumengeite.

Boracite.—X-Ray examination of boracite [55] throws a doubt on the usually accepted formula $Mg_7Cl_2B_{16}O_{30}$ (of W. Heintz, 1859). The rhombic-dodecahedral crystals are built up of twelve orthorhombic hemimorphic pyramids in such a manner that the twelve (100) faces give the external faces of the composite crystal. The optic axial plane is parallel to the longer diagonal and the polar c-axes are parallel to the shorter diagonal of a dodecahedral face. The positive ends of the polar axes are directed towards alternate pseudo-triad axes, and this gives rise to the well-known pyroelectric properties of the mineral. X-Ray measurements gave for the unit cell dimensions of colourless crystals (d 2·92—2·97) $a = b = 16·97$, $c = 12·00$ Å.; and for greenish crystals (d 2·97—3·10) containing some ferrous iron $a = b = 17·11$, $c = 12·10$ Å. This would give seven (or 7·3) molecules of $Mg_7Cl_2B_{16}O_{30}$ in the unit base-centred cell, which from considerations of symmetry is improbable. A new analysis leads to a formula $Mg_{25}Cl_8B_{56}O_{105}$; or more simply $Mg_6Cl_2B_{14}O_{26}$, eight (7·845) molecules of which can be accommodated in the unit cell. It would be of interest to determine by X-ray

[53] B. Gossner, *Amer. Min.*, 1928, **13**, 580; *A.*, 749.

[54] B. Gossner and M. Arm, *Z. Krist.*, 1929, **72**, 202.

[55] J. W. Gruner, *Amer. Min.*, 1928, **13**, 481; *Amer. J. Sci.*, 1929, [v], **17**, 453; *A.*, 749.

methods whether the structure is truly cubic at a temperature above 265°.

Domeykite Group.—The several copper arsenide minerals from Michigan have been examined by X-ray methods and by the metallographic method on polished surfaces under the microscope. L. S. Ramsdell[56] finds that domeykite (Cu_3As) is a definite compound, but it gives a different X-ray pattern from that given by artificial Cu_3As obtained with fused mixtures of copper and arsenic; when heated, however, it changes into a form corresponding with the artificial product. Algodonite (Cu_6As) is also found to be a definite compound, although it cannot be prepared artificially in fusions; when heated, it breaks down into a mixture of Cu_3As and Cu–As solution. Whitneyite (Cu_9As) is a mixture of algodonite and the Cu–As solutions. Arsenic up to 4% can be present in solid solution in copper. F. Machatschki[57] finds, on the other hand, that both algodonite and whitneyite are mixtures of : (1) a cubic substance which appears to be metallic copper contaminated with arsenic and has a lattice constant $a = 3\cdot647$—$3\cdot651$ Å.; and (2) a compound poorer in copper than Cu_6As, possessing the hexagonal type of close-packed structure with lattice constants $a = 2\cdot598$—$2\cdot599$, $c = 4\cdot213$—$4\cdot215$ Å.

Fahlerz Group.—X-Ray examination of tetrahedrite " from Hungary " by J. Palacios[58] gave a unit cell of edge $a = 10\cdot39$ Å. and containing eight molecules Cu_3SbS_3. W. F. de Jong[59] obtained for different specimens $a = 10\cdot190$—$10\cdot555$ Å., with eight molecules Cu_3SbS_{3-4} in the unit cell. F. Machatschki[60] also examined material from various localities and found for Cu–Sb fahlerz (tetra-hedrite) $a = 10\cdot32$ Å., which increases to $10\cdot41$ when much silver replaces copper, and decreases to $10\cdot19$ in tennantite when arsenic takes the place of antimony in the formula $R^I_3R^{III}S_3$. These authors are all agreed in rejecting the old formula $4Cu_2S,Sb_2S_3$, but they take no account of the bivalent metals, principally iron and zinc, which are almost invariably present in fahlerz. This mineral shows, in fact, a wide range in chemical composition and in density; but not in a single case were these determined for the materials used for the X-ray analysis. V. V. Nikitin[61] points out a similarity in the atomic structure suggested by Machatschki for fahlerz with those of chalcopyrite and zinc-blende; and he also emphasises the fact that these minerals are often found in parallel growth on crystals of

[56] *Amer. Min.*, 1929, **14**, 188; *A.*, 1264.

[57] *Jahrb. Min., Beil.-Bd.*, 1929, [*A*], **59**, 137.

[58] *Anal. Fís. Quím.*, 1927, **25**, 248; *A.*, 1927, 1015.

[59] Proefschrift, Delft, 1928.

[60] *Norsk Geol. Tidsskr.*, 1928, **10**, 23; *Z. Krist.*, 1928, **68**, 204; *A.*, 1928, 1080.   [61] *Z. Krist.*, 1929, **69**, 482; *A.*, 1263.

fahlerz, due to the similarity, not only of structure, but also of molecular volume. He makes the interesting suggestion that molecules of zinc-blende, chalcopyrite ($CuFeS_2$), and perhaps metacinnabarite (HgS), may be present in solid solution or even very finely disseminated in the fahlerz substance. This seems to afford a satisfactory explanation of the departure of analyses from the ideal formula Cu_3SbS_3.

Spinel.—Certain artificial gem spinels differ from ordinary spinel in containing a large excess of alumina over that required by the spinel formula $MgAl_2O_4$. These have been studied in detail by F. Rinne [62] by all the available methods. Each pear-shaped drop is a single crystal and shows rounded faces of the cube, octahedron, and rhombic-dodecahedron, and the silky upper surface shows a minute reticulated crystalline pattern. The axis of the pear, corresponding with the direction of growth under the oxyhydrogen blow-pipe, usually coincides with a cubic axis of the crystal. X-Ray examination by the Laue, rotating-crystal, and powder methods shows no essential difference between these artificial spinels of variable composition and natural spinel; and the powder photographs are the same as those given by γ-Al_2O_3. The following table gives a selection of the determined data :

Composition.	Sp. gr.	n_D.	Edge a of unit cube.
MgO,Al_2O_3	3·577	1·7190	8·02 Å.
$MgO,1·7Al_2O_3$	3·604	1·7239	—
$MgO,3·3Al_2O_3$	3·620	1·7272	7·96
$MgO,4Al_2O_3$	3·625	1·7284	7·92
$MgO,5Al_2O_3$	—	1·7288	7·91

The conclusion reached is that the material consists of a solid solution or mixed crystal of γ-Al_2O_3 in spinel. When spinels that contain an excess of alumina are tempered for some hours at 800° they become cloudy and show a moonstone schiller and asterism, due, as shown under the ultra-microscope, to the separation of minute particles. Tempered for longer periods, the stones become opaque; the Lauegrams then show two series of spots, and thin sections under the microscope show a regular network intergrowth of spinel and corundum. This change is accompanied by an increase in density from 3·62 to 3·81, corresponding with the inversion of γ-Al_2O_3 to α-Al_2O_3 (corundum).

Sources of Supply of the Less Common Elements.

Practical uses for more and more elements are gradually becoming known. Detailed accounts of the modes of occurrence and the

[62] *Jahrb. Min., Beil.-Bd.*, 1928, [*A*], **58**, 43; *A.*, 1928, 730. See also P. F. Kerr, *Amer. Min.*, 1929, **14**, 259.

precise localities where the rarer minerals have been found, often by chance, have been recorded in mineralogical literature in a more or less haphazard manner.   When any particular element is discovered to have some economic application, there is an immediate call for it, and the mineralogical records, if made available by suitable indexes, should then be of some use.   Even for the abundant elements, such as aluminium, a knowledge of the various modes of occurrence and distribution of its several minerals, such as cryolite and bauxite, is of importance.

For the elements already in practical use this aspect of the subject is dealt with in several books on economic geology and ore deposits. A book collecting together the scattered information on the geochemical distribution of the chemical elements has recently been compiled by G. Berg, " Vorkommen und Geochemie der mineralischen Rohstoffe " (Leipzig, 1929); and another dealing more with general principles by F. Behrend and G. Berg, " Chemische Geologie " (Stuttgart, 1927).

Beryllium.—In view of the possible use of light and strong alloys of aluminium and beryllium in aeronautics, there have been many inquiries for sources of this element.   Beryl, the most abundant beryllium mineral (Be about 5%), usually occurs as isolated crystals in certain pegmatite veins, large crystals being occasionally found in the felspar quarries of the south of Norway, and larger crystals weighing one or two tons have been found in New Hampshire.   A recent find of large crystals is reported from Namaqualand, South Africa, and a beryl deposit is worked for emeralds of gem quality in the Leydsdorp district, north-eastern Transvaal.[63]   A new find of massive white beryl, apparently in considerable quantity, is reported in the Masull ravine, near Merano in Trentino.[64]   Other minerals containing a higher percentage of the metal, namely, hambergite (Be 19%), phenakite (16½%), bertrandite (15%), beryllonite (7%), chrysoberyl (7%), and euclase (6%), are of more sparing occurrence; while bromellite, BeO (*Ann. Reports*, 1925, **22**, 277), is known only as a few minute crystals.   The old felspar quarry near Písek in Bohemia, which has yielded a variety of beryllium minerals, has recently been reopened.[65]   A list of localities where beryllium minerals have been found is given by M. Hosenfeld.[66]

Bromine.—Carnallite from Solikamsk, govt. Perm, Russia, contains 0·17—0·30% of bromine, apparently present as a double salt

[63] J. M. Le Grange, *Trans. Geol. Soc. S. Africa*, 1930, **32** (for 1929).

[64] E. Dittler, *Tsch. Min. Petr. Mitt.*, 1929, **40**, 188.

[65] J. V. Želízko, *Věstnik Státního Geol. Ústavu Československé Republiky*, 1928, **4**, 23.

[66] *Wiss. Veröff. Siemens-Konz.*, 1929, **8**, [1], 21; *B.*, 722.

$KCl,MgBr_2,6H_2O$. Large amounts appear to be available.[67] A pamphlet on the production and occurrence of bromine has been issued in the series " The Mineral Industry of the British Empire and Foreign Countries " (Imperial Institute, London, 1928).

Cæsium.—The main source of cæsium, now used in thermionic valves, is the mineral pollucite (Cs_2O 34%). This has been produced in some quantity from the felspar quarries in pegmatite at Andover and other localities in Maine, U.S.A.[68] In general appearance, pollucite is very similar to quartz, and perhaps it has been overlooked in some other pegmatites. Other cæsium-bearing minerals are cæsium-beryl, rhodizite, and lepidolite; the last, when mined for lithium, may come to be of importance as a source of cæsium. Lepidolite from South-West Africa was found to contain Cs_2O 0·60% with Rb_2O 1·73%.[69]

Germanium.—Many minerals have been examined spectrographically for germanium.[70] Traces were found in the tin ores cassiterite and stannite, in zinc ores, native copper, and various silicates. Apart from the germanium mineral argyrodite, and germanite, the largest amount (0·1%) was found in enargite from Mexico.

Gallium.—Various minerals have been examined spectrographically for gallium. Lepidolite from California[71] yielded 0·007% of the metal, and a green kaolin[72] from Japan had contents of the order 0·0004—0·004%.

Hafnium.—A review of the mineralogy of hafnium has been given by O. I. Lee.[73] In zirconium minerals the ratio $HfO_2 : ZrO_2$ varies from 0·007 to 0·5 with an average of 0·02.[74] In zircon, the content of hafnium appears to increase with the radioactivity (due to traces of thorium and uranium), and altered zircons (alvite and crytolite) are richer than unaltered.

Iodine.—In small amounts iodine is of wide distribution (*Ann. Reports*, 1927, 24, 294). It is recorded (I 0·13%) in the saline encrustations of Vesuvius,[75] in the gases escaping from various

[67] N. N. Efremov and A. A. Veselovski, *J. Chem. Ind. Moscow*, 1928, 5, 1365: *A.*, 1163.

[68] E. E. Fairbanks, *Amer. Min.*, 1928, 13, 21.

[69] J. Jakob, *Schweiz. Min. Petr. Mitt.*, 1927, 7, 139; *A.*, 45.

[70] J. Papish, F. M. Brewer, and D. A. Holt, *J. Amer. Chem. Soc.*, 1927, 49, 3028; *A.*, 1928, 146; J. Papish, *Econ. Geol.*, 1928, 23, 660; 1929, 24, 470.

[71] J. Papish and D. A. Holt, *J. Physical Chem.*, 1928, 32, 142; *A.*, 1928, 265.

[72] S. Iimori, *Sci. Papers Inst. Phys. Chem. Res. Tokyo* (Supplement), 1929, 10, No. 8; *A.*, 420.

[73] *Chem. Reviews*, 1928, 5, 17.

[74] G. von Hevesy and K. Würstlin, *Z. physikal. Chem.*, 1928, 139, 605; *A.*, 288.

[75] L. Coniglio, *Ann. R. Osservatorio Vesuviano*, 1925, [iii], 2, 123.

mineral springs,[76] and in rock phosphates.[77]   A pamphlet on the production and occurrence of iodine has been issued in the series "The Mineral Industry of the British Empire and Foreign Countries" (Imperial Institute, London, 1928).

Lithium.—Lithium minerals, lepidolite, spodumene, and amblygonite, are found in considerable quantities at several places in the Oiseau River district in Manitoba.[78]

Radium.—A report dealing with the uses of radium, more especially for medical treatment, and with its production and sources of supply has been issued by the Radium Sub-Committee of the Committee of Civil Research (London, 1929).   The production from the western American carnotite fell from $35\frac{1}{2}$ g. of radium element in 1921 to 12 g. in 1923 and has now ceased.   The present restricted supply is obtained from the richer uranium ore associated with copper ores in Katanga, Belgian Congo.   A recent discovery of pitchblende in the Gordonia district of Cape Province as isolated crystals (uraninite) in pegmatite is less promising than would be a lode deposit with large mammillated masses of pitchblende.   The copper belt now being explored in Northern Rhodesia is perhaps a likely place for future developments.   All igneous rocks contain minute amounts of radium; for example, C. S. Piggot[79] finds in granites from the eastern United States from 0.378 to 4.826×10^{-12} g. of radium per gram of rock.

Rubidium.—A method for the extraction of rubidium salts from carnallite has been given by G. Jander and H. Faber.[80]   J. Jakob[69] records the presence of Rb_2O 1.73% in lepidolite from South-West Africa, and 1.16% has been found in lepidolite from Japan.[81]

Ruthenium.—This is present as a minor constituent of pink kaolin from Tanokami, Japan, the colour of which is supposed to be due to the presence of rhodium and ruthenium.[82]

Selenium.—The use of photo-sensitive cells for television and the transmission of pictures is calling for an increased supply of this element.   A new occurrence of selenium minerals has been found in the Roter Bär mine at Andreasberg in the Harz Mountains,

[76] T. von Fellenberg, *Biochem. Z.*, 1928, **193**, 384; *A.*, 1928, 611.

[77] E. Wilke-Dörfurt, J. Beck, and G. Plepp, *Z. anorg. Chem.*, 1928, **172**, 344; *A.*, 1928, 864.

[78] J. S. De Lury, *Industrial Development Board of Manitoba, Winnipeg*, 1927.

[79] *Amer. J. Sci.*, 1929, [5], **17**, 13; *A.*, 1036.

[80] *Z. anorg. Chem.*, 1929, **127**, 321.

[81] S. Iimori and J. Yoshimura, *Bull. Chem. Soc. Japan*, 1926, **1**, 237; *A.*, 1927, 129.

[82] *Idem, ibid.*, 1929, **4**, 1; *A.*, 420.

analyses of the picked ore showing Se 24—27%.[83] The selenium ores from the earlier known occurrences in the Harz Mountains [84] have been studied by the metallographic method in polished sections under the microscope.[85] A new selenium mineral has been detected, and named klockmannite (CuSe),[86] in intimate association with the umangite (Cu_3Se_2) of the Sierra de Umango in Argentina, Lehrbach in the Harz Mountains, and at Skrikerum in Sweden. Selenium in a form soluble in water, perhaps as selenious acid or as an alkali selenite, has been found in saline encrustations (Se 1·25% with Te 0·04%) in the crater of Vesuvius.[87]

New Minerals.

An eleventh dictionary list of new mineral names for the period 1926—1928 gives 190 names, several of which are merely synonyms or of little value.[88] Some rare minerals of the platinum group, of which a preliminary mention was made in the last report (1927, **24**, 311) have now been more fully described. Potarite, PdHg, discovered by the late Sir John Harrison, crystallises as octahedra in the cubic system.[89] Palladium antimonide, Pd_3Sb, from the Transvaal platinum fields has been named stibiopalladinite.[90] Another new platinum mineral from the same district is listed below under the name cooperite. Several new crystallised iron sulphates are described from a mine in Arizona, where a body of pyritic ore had been burning underground for some years; they were probably formed when the mine was flooded with water in the attempts to extinguish the fire.[91]

Bismutotantalite,[92] tantalate (and niobate) of bismuth, $Bi_2O_3,(Ta,Nb)_2O_5$, as large orthorhombic crystals in a pegmatite vein on Gamba Hill, Uganda. Analyses show Bi_2O_3 about 50%,

[83] H. Rose, *Fortschr. Min. Krist. Petr.*, 1927, **12**, 72; W. Geilmann and H. Rose, *Jahrb. Min., Beil.-Bd.*, 1928, [*A*], **57**, 785.

[84] Selenium was extracted on a moderately large scale from these ores at Tilkerode in the eastern Harz a hundred years ago, and the product appears to have been marketed in the form of small medallions showing in relief a bust of Berzelius. Examples of these are preserved in the apartments of the Chemical Society and in the Mineral Department of the British Museum (L. J. Spencer, *Min. Mag.*, 1928, **21**, 404).

[85] G. Frebold, *Centr. Min.*, [*A*], 1927, 16, 196.

[86] P. Ramdohr, *Centr. Min.*, [*A*], 1928, 225; *A.*, 289.

[87] F. Zambonini and L. Coniglio, *Ann. R. Osservatorio Vesuviano*, 1925, [iii], **2**, 3.

[88] L. J. Spencer, *Min. Mag.*, 1928, **21**, 556.

[89] *Idem, ibid.*, p. 397; *A.*, 1928, 612.

[90] P. A. Wagner, "The Platinum Deposits and Mines of South Africa," Edinburgh and London, 1929, p. 12; H. Schneiderhöhn, *Centr. Min.*, [*A*], 1929, 193.

[91] C. Lausen, *Amer. Min.*, 1928, **13**, 203.

[92] E. J. Wayland and L. J. Spencer, *Min. Mag.*, 1929, **22**, 185.

Ta_2O_5 31—41%, Nb_2O_5 14—6%, and the mineral is analogous to stibiotantalite ($Sb_2Ta_2O_8$). If the formula is written as $(BiO)_2Ta_2O_6$ and the axial ratios are readjusted, the mineral shows a close relation to tantalite ($Fe_2Ta_2O_6$). The black crystals are in part altered to a pinkish-yellow hydrated material which seems to consist of a mixture of two minerals.

Cooperite, [90, 93] sulpharsenide of platinum, $Pt(As,S)_2$, as minute steel-grey fragments and rectangular rods found in the concentrates from the platiniferous norites and dunites of the Bushveld, Transvaal. Examined by reflected polarised light, it is seen to be anisotropic and probably orthorhombic. It presumably belongs to the marcasite group and is dimorphous with sperrylite ($PtAs_2$). Like sperrylite, it is attacked neither by aqua regia nor by nascent chlorine (when the mineral is treated with solid potassium chlorate and hydrochloric acid). After ignition the material yields to aqua regia.

Gudmundite,[94] sulphantimonide of iron, $FeSbS$, as small silver-white to steel-grey crystals embedded in calcite. The orthorhombic crystals are isomorphous with mispickel ($FeAsS$), and the two minerals, very similar in appearance, are associated together in the lead and zinc ore at Gudmundstrop, near Sala, Sweden.

Hydrothorite,[95] hydrous thorium silicate, $ThSiO_4,4H_2O$, occurring, together with thorogummite and pilbarite, as an alteration product of mackintoshite in a pegmatite vein at Wodgina, Western Australia. It is pale pink or cream-coloured, earthy, and very friable, and is optically isotropic.

Larnite,[96] calcium orthosilicate, occurring as a constituent of a metamorphic rock at the contact of chalk and dolerite near Larne in County Antrim. The finely granular rock shows an unusual assemblage of minerals, including spurrite ($2Ca_2SiO_4,CaCO_3$), larnite (Ca_2SiO_4), merwinite ($3CaO,MgO,2SiO_2$), gehlenite, spinel, and calcite. Larnite is monoclinic with optical characters agreeing with those of the artificial $\alpha\text{-}Ca_2SiO_4$. When the larnite rock is heated to dull redness and allowed to cool, it falls to powder, due to the inversion to $\gamma\text{-}Ca_2SiO_4$.

Larsenite and *Calcium-larsenite*.[97] These two minerals occur in veinlets in the massive zinc ore at Franklin Furnace, New Jersey. Larsenite is an orthosilicate of lead and zinc, $PbZnSiO_4$, and forms

[93] R. A. Cooper, *J. Chem. Met. Min. Soc. S. Africa*, 1928, **28**, 281; *A.*, 1928, 1111.

[94] K. Johansson, *Z. Krist.*, 1928, **68**, 87; *A.*, 788.

[95] E. S. Simpson, *J. Roy. Soc. W. Australia*, 1928, **13** (for 1927), 37.

[96] C. E. Tilley, *Min. Mag.*, 1929, **22**, 77; *A.*, 787.

[97] C. Palache, L. H. Bauer, and H. Berman, *Amer. Min.*, 1928, **13**, 142, 334; *A.*, 787.

colourless orthorhombic prisms isomorphous with olivine. In calcium-larsenite about half of the lead is replaced by calcium, the formula being $(Pb,Ca)ZnSiO_4$. This massive white mineral is remarkable in showing a brilliant lemon-yellow fluorescence when exposed to ultra-violet rays. It is intimately associated with willemite, hardystonite, and clinohedrite, and in the mass these minerals are scarcely distinguishable, but in the ultra-violet rays they show fluorescent glows respectively brilliant green, violet, and orange-red.[98] This property enabled pure material to be selected for analysis. Larsenite displays a pale violet fluorescence.

Mitscherlichite,[99] hydrous double chloride of potassium and copper, $K_2CuCl_4,2H_2O$, as minute greenish-blue crystals on the surface of a saline stalactite from the floor of the crater of Vesuvius. The crystals are tetragonal like those of the artificial salt prepared by E. Mitscherlich in 1840.

Nahcolite,[1] sodium hydrogen carbonate, not previously definitely recognised as a mineral, is so named from the formula $NaHCO_3$, to distinguish it from the other sodium carbonate minerals. It occurs as a constituent of a white crystalline saline encrustation found in 1888 on the walls of a Roman conduit at the Baths of Nero, which was exposed during the construction of the railway line from Baia to Naples. When the conduit was opened the contained atmosphere was highly charged with carbon dioxide. Analysis of the material shows varying amounts of sodium carbonate and sulphate with 7·48—8·45% of H_2O, and they are interpreted as mixtures of thermonatrite (Na_2CO_3,H_2O), trona $(Na_2CO_3,NaHCO_3,2H_2O)$, nahcolite $(NaHCO_3)$, and thenardite (Na_2SO_4), each of which was also determined by its optical characters.

Probertite,[2] hydrous borate of sodium and calcium,
$$Na_2CaB_6O_{11},6H_2O,$$
as rosettes of glassy columnar monoclinic crystals embedded in kernite and secondary borax in the Kramer district, Kern Co., California. Probertite (also known as kramerite) and kernite (or rasorite) are the primary minerals in a lode-like deposit formed by hot springs in Miocene beds. Secondary minerals derived from them are borax and ulexite.
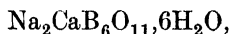
L. J. SPENCER.

[98] C. Palache, *Amer. Min.*, 1928, **13**, 330; L. J. Spencer, *ibid.*, 1929, **14**, 33.

[99] F. Zambonini and G. Carobbi, *Ann. R. Osservatorio Vesuviano*, 1925, [iii], **2**, 7.

[1] F. A. Bannister, *Min. Mag.*, 1929, **22**, 53; *A.*, 535.

[2] A. S. Eakle, *Amer. Min.*, 1929, **14**, 427.

CRYSTALLOGRAPHY.

THE year 1929 has been remarkable not so much for new discoveries as for the systematic arrangement of the results of previous researches, so that the subject of Crystallochemistry has already taken very definite shape. The lead given by V. M. Goldschmidt has been followed with success. One of the outstanding events of the year was the meeting of the Faraday Society on the occasion of his lecture. The papers and discussion at this meeting, which is the first international meeting of X-ray crystallographers, have been collected in " Crystal Structure and Chemical Constitution," [1] which gives an excellent picture of the present state of the subject.

At the same time a conference was held under the auspices of Sir William Bragg at the Royal Institution, at which the question of notation and methods of publication of crystal structures were discussed and committees set up for proposing means for standardising and improving them. It is to be hoped that ways will be found of making the results of structural analysis more intelligible and more generally available.

New Books.—" Kristallographische und Strukturtheoretische Grundbegriffe," [2] by P. Niggli, gives a very complete account of the geometrical basis of crystal structure. The particular contribution of Niggli, which follows the tradition of Schoenflies and Fedorov and brings it up to date by the consideration of individual atomic domains, has not yet found very much application in practice, but it is bound to do so when detailed experimental investigations have been co-ordinated into general systems.

" Röntgenspectroscopie und Kristallstrukturanalyse," [3] by A. Scheede and E. Schneider, is another complete text-book of X-ray crystallography, particularly valuable for its accounts of chemical analysis by emission and absorption spectra.

" Cristallographie Géometrique," [4] by H. Bouasse, gives a comprehensive account of classical crystallography and the derivation of space-groups. The determination of crystal structure by means of X-rays is treated rather superficially, but most aspects of the work are covered.

[1] Published by the Faraday Society.
[2] " Handbuch der Experimentalphysik," Band VII, I Teil, Akademische Verlagsgesellschaft m.b.H., Leipzig.
[3] de Gruyter, Berlin.   [4] Paris, Librairie Delagrave,

" Zur Nomenklatur der 32 Kristallklassen," by Friedrich Rinne;
" Über ein neue Herleitung und Nomenklatur der 230 Kristallograph-
ischen Raumgruppen," [5] by Ernst Schiebold, with an atlas of the
230 space-groups containing 313 uncoloured and 36 coloured plates.
A discussion of this latest contribution to the systematics of space-
groups will have to be postponed to a later Report. The coloured
plates have an undoubted advantage in enabling complicated space-
groups to be easily grasped.

" A Summary of Published Information on X-Ray Investigation
of Alloys " [7] (1921—1928), by (Miss) C. F. Elam, contains all the
relevant data on alloy structures except the details of complicated
structures.

The " Strukturbericht " of the *Zeitschrift für Kristallographie* has
now completed its account of inorganic crystals, except metals,
and is already an indispensable work of reference.

Less than half of the relevant papers (over 400) which have
appeared during the year can be mentioned here. Four branches
of crystal physics, *viz.*, magnetic properties of crystals, X-ray optics,
electron diffraction in crystals, and the Raman effect in crystals,
are first dealt with; then follows a systematic account of crystal
structures determined during the last year; and finally a discussion
of X-ray diffraction in liquids.

The Magnetic Properties of Crystals.

This is one of the branches of crystal physics which are developing
very rapidly. It has long been known that the diamagnetic suscepti-
bility varies considerably with direction in the crystal, but it has
fallen to the Indian workers to show how this variation is related
to the arrangement of the ionic or molecular groups in the crystal
lattice. In the carbonates and nitrates [8] of the alkali and alkaline-
earth metals the direction of the maximum diamagnetic suscepti-
bility is always perpendicular to the plane of the carbonate or nitrate
radicals; and for those aromatic compounds whose crystal structure
is known, the striking fact emerges that the direction of maximum
susceptibility is perpendicular to the plane of the benzene ring.[9, 10]
Hexamethylbenzene is of particular interest because its crystal
structure has been accurately determined by means of X-rays [11]

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[5] Abhandlungen der math.-phys. Klasse der Sächs. Akad. der Wiss., Band
40, No. V, Schlussheft. Verlag von S. Hirzel, Leipzig, 1929.

[7] *J. Inst. Metals*, 1929, **41**, 329.

[8] K. S. Krishnan and (Sir) C. V. Raman, *Proc. Roy. Soc.*, 1927, [*A*], **115**,
549; *A.*, 1927, 925.

[9] S. Bhagavantam, *ibid.*, 1929, [*A*], **124**, 545; *A.*, 982.

[10] *Idem*, *Indian J. Physics*, 1929, **4**, 1; *A.*, 1133.

[11] (Mrs.) K. Lonsdale, *Proc. Roy. Soc.*, 1929, [*A*], **123**, 494; *A.*, 750.

(see p. 304), so that the orientation of the flat benzene ring relative to the crystal lattice is known with certainty. The magnetic properties of this substance have now been determined [12] and are found to accord with the above generalisation. It is also important that in the plane of the ring the magnetic and optical properties agree in showing a slight anisotropy. It is clear that a knowledge of the directions of maximum and minimum susceptibility in the case of such compounds affords valuable evidence as to the truth of their crystal structure determined by means of X-rays. The values of the magnetic anisotropy in some aromatic compounds are quite remarkable; for example, in naphthalene the susceptibility perpendicular to the plane of the benzene ring is four times that parallel to it, and in graphite the susceptibility perpendicular to the cleavage plane, which is parallel to the net of the benzene ring, is seven times [13] that parallel to it. The aliphatic compounds have an altogether smaller magnetic anisotropy,[10] and as yet no general relation between the characteristic grouping of the carbon chains and the magnetic properties has emerged.

The magnetostriction of bismuth has been discovered by Kapitza,[14] who has shown that a rod placed parallel to the magnetic field expands when it is grown parallel to the trigonal axis but contracts if grown at right angles to it. This is the first diamagnetic substance in which magnetostriction has been observed, and the effect is remarkable by reason of its large magnitude, being greater than that of iron. It also shows that the binding forces between the atoms of crystals can be modified considerably by a very strong magnetic field. The magnetic susceptibilities of single crystals of bismuth and antimony parallel to and perpendicular to the principal axis have also been measured.[15]

Investigations on the magnetic properties of ferromagnetic substances have received a great impulse from the development of the technique of preparing single crystals of metals : those of iron, nickel, and cobalt may be obtained of such a size that a cube of about 5 cm. side may be cut out from the matrix.[16] The magnetisation both parallel to and perpendicular to the field in various directions on plates cut parallel to the faces (100), (110), and (111) of these crystals has been determined.[16, 17] Single crystals of zinc and

[12] S. Bhagavantam, *Proc. Roy. Soc.*, 1929, [*A*], **126**, 143.

[13] (Sir) C. V. Raman, *Nature*, 1929, **123**, 945; *A.*, 871.

[14] P. Kapitza, *ibid.*, **124**, 53; *A.*, 989.

[15] O. Nusbaum, *Physical Rev.*, 1927, [ii], **29**, 905; *A.*, 1928, 1314.

[16] S. Kaya, *Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 640; *A.*, 1928, 1081.

[17] K. Honda and S. Kaya, *ibid.*, 1926, **15**, 721; *A.*, 1927, 298; S. Kaya, *ibid.*, 1928, **17**, 1157; *A.*, 633; W. L. Webster, *Proc. Roy. Soc.*, 1925, [*A*], **107**, 496; *A.*, 1925, ii, 369; W. Sucksmith, H. H. Potter, and L. Broadway, *ibid.*, 1928, [*A*], **117**, 471; *A.*, 1928, 110; K. Beck, *Diss.*, Zurich, 1918; see also *Bull. Nat. Res. Council*, 1922, **3**, 180.

cadmium [18] have been similarly prepared and investigated. The results are more complicated than those obtained with polycrystalline rods and plates, and show the intimate relation which exists between the magnetic properties and the crystal structure. The variation of the magnetisation of iron with temperature [19] up to the Curie point has been studied. The magnetostriction [20] and magnetoresistance [21] effects have now been investigated as comprehensively as the magnetisation for both iron and nickel, so that full experimental data are now available as to the magnetic properties of these two metals and of cobalt.

Theoretical research on ferromagnetism is also proceeding rapidly, but on quite different axioms from those employed formerly. The older theories [22] of ferromagnetism, although giving a general descriptive, and in some cases quantitative, account of the directional properties of single ferromagnetic crystals, did not throw any light on the origin of the phenomenon. The new theory of W. Heisenberg [23] employs only the fundamental conceptions of quantum mechanics and shows that ferromagnetism arises from the exchange degeneracy of the electrons in the different electronic systems of the lattice. The theory can only be said to have just begun, and O. von Auwers,[24] in a critical review of the crystallographic and magnetic data of ferromagnetic elements and compounds, points out its failures and limitations. It is a much more fundamental theory than its predecessors and is already being developed so as to include more of the phenomena of ferromagnetism. R. H. Fowler and P. Kapitza [25] have successfully applied it to determine the change of specific heat at the Curie point and the change of size produced during magnetostriction.

Faraday showed that when transparent substances were placed in a strong magnetic field and a beam of plane-polarised light was passed through them, a small rotation of the plane of polarisation occurred. The effect is generally very small, but Becquerel showed

[18] J. C. McLennan, R. Ruedy, and (Miss) E. Cohen, *Proc. Roy. Soc.*, 1928, [*A*], **121**, 9; *A.*, 19.

[19] K. Honda, H. Masumoto, and S. Kaya, *Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 111; *A.*, 1928, 823.

[20] K. Honda and Y. Masiyama, *ibid.*, 1926, **15**, 755; *A.*, 1927, 299; W. L. Webster, *Proc. Roy. Soc.*, 1925, [*A*], **109**, 570; Y. Masiyama, *Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 945; *A.*, 19.

[21] W. L. Webster, *Proc. Roy. Soc.*, 1926, [*A*], **113**, 196; 1927, [*A*], **114**, 611; *A.*, 1927, 11, 505; S. Kaya, *Sci. Rep. Tôhoku Imp. Univ.*, 1928, **17**, 1027; *A.*, 20.

[22] K. Honda and Junzo Okubo, *ibid.*, 1916, **5**, 153; G. S. Mahajani, *Phil. Trans.*, 1929, [*A*], **228**, 63; *A.*, 495.

[23] *Z. Physik*, 1928, **49**, 619; *A.*, 1928, 1300.

[24] *Physikal. Z.*, 1928, **29**, 921; *A.*, 127.

[25] *Proc. Roy. Soc.*, 1929, [*A*], **124**, 1; *A.*, 751.

that in certain crystals, namely, tysonite (Ce,La,Di,)F_3, parisite (CaF)(CeF)Ce$(CO_3)_3$, and bastnasite (Ce,La,Di)$_2$$(CO_3)_3(Ce,La,Di)F_3$, all containing rare-earth elements, relatively enormous rotations occurred.   J. Becquerel and W. J. de Haas [26] have continued the investigation, and the following is given as an example of the magnitude of the rotation : at a temperature of 1·95° K., and for a thickness of 1 mm. with wave-length 3830 Å., and a magnetic field of 26·7 kilogauss, the rotation is 18·26 π.   The saturation value of the rotation is more easily obtained at low temperatures, since the rotation obeys the law $\rho/\rho_\infty = \tanh \Sigma_\infty H/RT$, where ρ_∞ is the saturation value of the rotation and Σ_r is a constant.   The value of Σ_∞ is found to be one Bohr magneton, showing that only one electron is responsible for the magnetic rotation.   The active ion has been shown [27] to be Ce''', with which is associated an intense absorption band at 3270 Å.   At low temperatures the absorption bands become extremely fine, showing a well-marked Zeeman effect,[28] and Becquerel has put forward a tentative theory to account for this group of interesting phenomena.

X-Ray Optics.

In one of the most interesting papers of the year on X-ray optics, W. L. Bragg [29] shows the close resemblance between the formation by a lens of a real image of an object and the derivation of the structure of a crystal from the scattered beams of X-rays, and gives the mathematics uniting all the information involved.   The work is essentially an extension of the Abbé theory of microscopic vision to the scattering of X-rays by a crystal grating.   We may suppose the formation of the real image by a lens to take place in the following stages.   (The object is supposed for the sake of simplicity to consist of a simple line-grating illuminated by a parallel beam normal to the grating.)   Spectra of several orders will be produced and brought to foci in the focal plane of the lens.   These spectra having the appropriate phase relations may be considered as light-sources which suffer mutual interference with the production of the image of the object.   The greater the number of the spectra in the focal plane of the lens which contribute to the final image, the more faithful is its representation of the object.   When a parallel beam of X-rays falls upon a crystal, we obtain experimentally only the first stage in the formation of the image, namely, the production of the separate spectra.   The reflexion of any plane has two properties,

[26] *J. Phys. Radium*, 1929, [vi], **10**, 283; *Z. Physik*, 1929, **57**, 11; *A.*, 1134.

[27] *Compt. rend.*, 1929, **188**, 1156; *A.*, 633.

[28] *J. Phys. Radium*, 1929, [vi], **10**, 313; *Z. Physik*, 1929, **58**, 205; *A.*, 1224.

[29] *Z. Krist.*, 1929, **70**, 475; *Brit. J. Radiology*, 1929, **2**, 65.

PLATE I
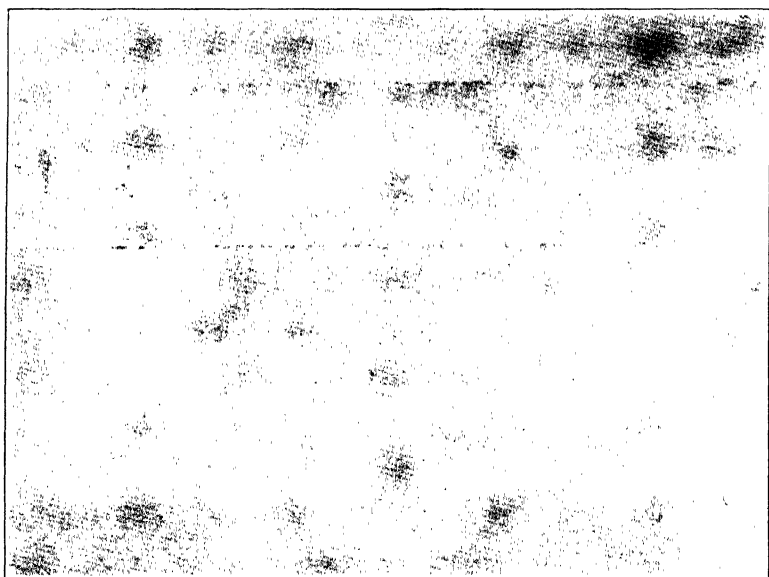
its deviation from the direction of the incident X-ray beam and its intensity, but it differs from the optical spectra in that it only occurs according to the Bragg law, *i.e.*, when the crystal is set in an appropriate position with respect to the incident X-rays. It is this last condition, apart from the difficulty of focusing X-rays, which makes it impossible to form an image of a crystal structure directly. If we consider two of the optical spectra which are symmetrical with respect to the undeviated beam, we see that they give rise in the plane of the image to interference bands. These are perpendicular to the line joining the spectra, spaced at intervals depending on the distance apart of the spectra, and of intensity proportional to that of the spectra. The X-ray spectra occur only one at a time, and hence, to obtain an image corresponding to the optical one, we must produce, optically or by mathematics, all the sets of interference fringes which would be produced if the X-ray spectra occurred all at once and could interfere with one another. Bragg carries out this process by photographing on the same print forty sets of black and white interference fringes oriented, spaced, and of such intensities that they imitate on a macroscopic scale those which would be produced by the X-ray spectra themselves. The result is a picture of the atoms of the crystal flattened down on to one plane—that perpendicular to the axis about which the crystal was rotated in obtaining the spectra. An example of such a photograph is given in Plate I, and the atomic arrangement which it represents in Fig.1. Such a visual synthesis of the crystal structure is of immense help in understanding the Fourier method of analysis, and a useful check on the results obtained by calculation. In another paper, Bragg gives the mathematical treatment of the same problem.[30] He extends R. J. Havighurst's method,[31] applicable to the distribution of atoms along a line in the structure, to their distribution over a plane. In Fig. 2, the results of such calculations for a plane normal to the c axis of diopside are plotted like a map, the contours indicating the electron density at any point. The fourteen parameters obtained by this method for diopside agree to within 0.5% with those calculated by the earlier method of W. L. Bragg and J. West.[32]

Fundamental in the study of the crystal structure is the knowledge of the scattering power of each kind of atom for X-rays of any wavelength. A wave-mechanical theory of scattering of X-rays by atoms and molecules has been added to the important papers on this subject.[33]

[30] *Proc. Roy. Soc.*, 1929, [*A*], **123**, 537; *A.*, 748.

[31] *J. Amer. Chem. Soc.*, 1926, **48**, 2113; *A.*, 1926, 995.

[32] *Z. Krist.*, 1928, **69**, 168; *Chem.-Zentr.*, 1929, i, 2013; *A.*, 1223.

[33] *Z. Physik*, 1928, **51**, 213.

Warnings to those who analyse crystal structures are to be found in two papers.   C. Mauguin [34] emphasises the fact that the X-ray analysis may sometimes be misleading if the crystal has a peculiar structure.   The families of the micas have almost the same structural unit in the plane of the cleavage independently of their composition,

Fig. 1.
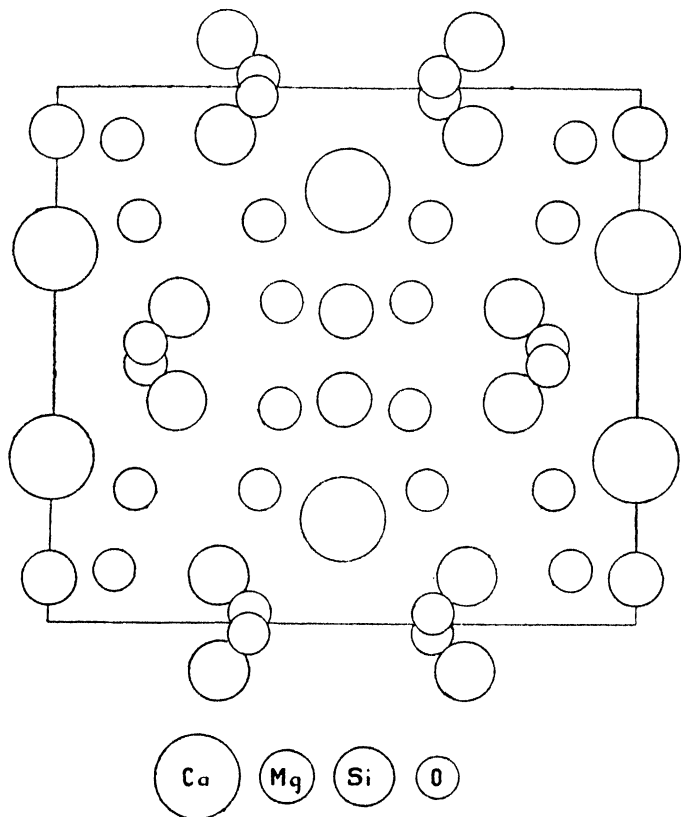
but there are two apparent exceptions in biotite and the chlorites. The exception cannot be real in the case of the latter because the direct interpretation of the X-ray results leads to the conclusion that there are 8/3 hydrogen atoms per unit cell, and we are forced to assume, in spite of X-ray data, a cell three times as large. Biotite forms an intermediate stage in the transition between the chlorites and the other micas. The rotation photographs obtained with

[34] *Compt. rend.*, 1928, **187,** 303.

chlorite show layer lines which correspond to a unit three times smaller than that of the other micas, *i.e.*, of the layer lines obtained with the other micas only every third occurs in the case of chlorite. In biotite also only every third occurs, but, instead of complete absence of spots in what would be the first and second layer lines, a faint continuous line is obtained. Mauguin interprets these results

FIG. 2.
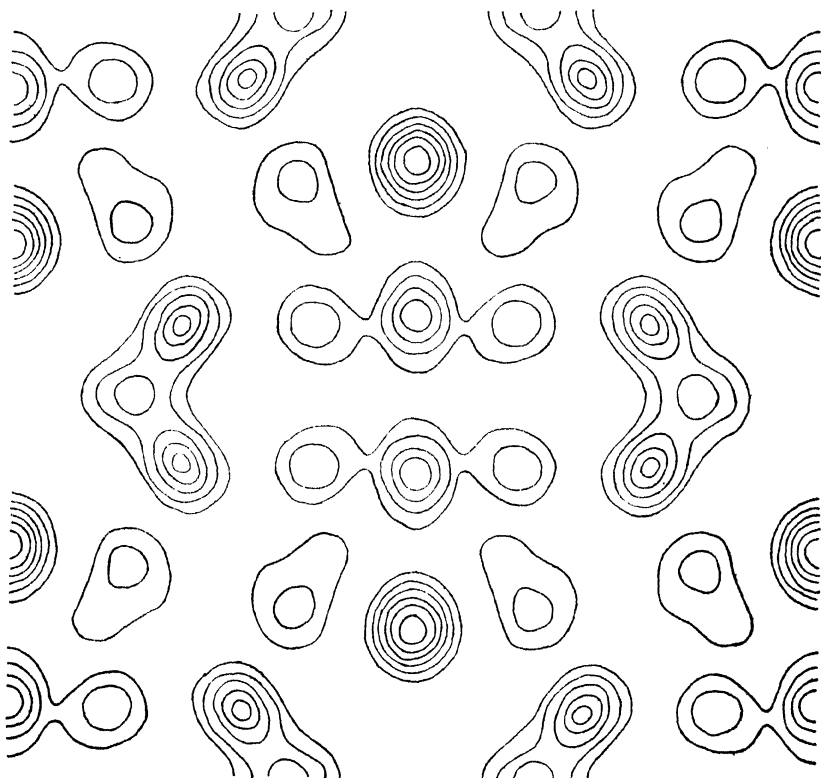
by supposing that the oxygen configuration is constant in all the micas, but that a slight rearrangement of the electropositive ions in the chlorites and biotites gives rise to these anomalies. W. Linnick [35] examined the photographs obtained by passing a beam of Cu-K radiation through a thin sheet of mica which had been heated to redness. The distribution of spots led him to suppose that the mica was behaving as a two-dimensional grating, and he believed that the heating had separated the cleavage flakes into such thin layers that they no longer behaved as a three-dimensional lattice.

[35] *Nature*, 1929, **123**, 604; *A.*, 492.

Bragg [36] showed that this assumption was quite unnecessary, for a slight rotation of the flakes relative to one another during the process of heating was sufficient to give rise to this effect : a rotation of $6\frac{1}{2}°$ is enough to give a pattern simulating that of the two-dimensional lattice because of the great length of the c-axis in mica. This is a good example of the difficulties which arise in the interpretation of photographs when one axis of the crystal is much greater than the other two.

Electron Diffraction in Crystals.

Perhaps the most striking discovery of recent years is the association of wave motion with moving material particles.   As early as 1924, L. de Broglie [37] showed on purely theoretical considerations that this association should occur, and that the wave-length would be given by the relation $\lambda = h/mv$, where h is Planck's constant, and mv the momentum of the particle.   If this formula is applied to the case of electrons, we find the wave-lengths characteristic of the electrons which have fallen through potential differences of 10, 100, 1000, and 10,000 volts to be 3·86, 1·22, 0·386, and 0·120 Å.U. respectively, corresponding to very soft, soft, hard, and very hard X-rays.   W. Elsasser [38] showed how de Broglie's predictions might be tested by allowing electrons of suitable velocity to fall on a single crystal of a metal and observing whether they were scattered in accordance with Bragg's law, just as in the case of X-rays.   C. J. Davisson and L. H. Germer [39] had been experimenting on the reflexion of electrons from a plate of nickel ; by accident their apparatus was broken and air admitted, and after the damage had been repaired the reflexion from the nickel was found to have been altered.   This was traced to changes in the crystalline state of the metal surface, and these authors therefore investigated the reflexion of electrons from a single crystal instead of from a polycrystalline aggregate.   A beam of electrons was made to fall normally on the crystal, and it was at once found that the deflected electrons were not diffusely scattered, as required by classical theory, but concentrated into a number of narrow beams whose orientation with respect to the crystal was quite in accord with its symmetry.   By assigning to the electrons the wave-length given by de Broglie's theory, they found that the reflected beams were approximately in the directions required by Bragg's law and the crystal structure.   The small but consistent deviation from Bragg's law was subsequently shown [40]

[36] Nature, 1929, 124, 125 ; A., 984.   [37] Compt. rend., 1924, 179, 39.
[38] Naturwiss., 1925, 13, 711.
[39] Physical Rev., 1927, 30, 705 ; A., 1928, 102.
[40] H. Bethe, Naturwiss., 1927, 15, 786 ; Ann. Physik, 1928, [iv], 87, 55 ; A., 1928, 677, 1303.

to be due to an accelerating potential of about 15 volts which acted upon the electrons as they entered the crystal. As the original velocity of the electrons was only about 50 volts, the effect of this boundary potential was very considerable, and when allowance had been made for it, the observations agreed very closely with the theory. Thus the association of a wave motion with moving particles was established by both theory and experiment, and the work of G. P. Thomson,[41] E. Rupp,[42] S. Kikuchi,[43] and others has amply confirmed this.

It will be realised that this discovery provides us with another technique whereby the structure of crystals may be investigated. Kikuchi has taken excellent photographs of electrons scattered by passing through the thinnest possible flake of mica with an exposure as short as 2 seconds. A triangular network of spots was obtained, and this pattern was interpreted as being due to the two-dimensional lattice of atoms in the net planes parallel to the cleavage. As the thickness is increased, the crystal begins to give a pattern corresponding to a three-dimensional lattice, some of the spots on the former pattern disappearing and others being enhanced. Finally, with a still greater thickness, a pattern is produced which is crossed by numbers of black and white lines. The first pattern is never obtained with X-rays, the second is the familiar Laue picture, but the third is quite peculiar to electron scattering. When the electrons fall on a fairly thick flake they are scattered several times before emerging on the other side, and we should therefore obtain the same result if we replaced the electron beam by a point source of electrons on the surface of the mica, radiating in all directions. In this case some electrons would always fall on every plane at the angle required for reflexion according to the Bragg law, and hence we should obtain black lines produced by the reflexion of electrons from the various planes. Where the electrons were reflected out of the main beam, there would be a deficiency giving rise to the white lines. Kikuchi has been able to show in a favourable case, such as that of mica, how the orientation and cell size of the structure may be determined, and the beginning of the next essential step has been made by G. P. Thomson in deriving the F curve for gold. There is every reason for believing that it will soon be possible to determine structures completely by this method.

Electrons are reflected in large quantity on passing through the

[41] *Proc. Roy. Soc.*, 1928, [*A*], **117**, 600; **119**, 651; 1929, [*A*], **125**, 352; *A.*, 1928, 3, 938; *A.*, 1209.
[42] *Physikal. Z.*, 1928, **29**, 837; *Ann. Physik*, 1929, [v], **1**, 773, 801; *A.*, 619.
[43] *Japan. J. Physics*, 1928, **5**, 83; *Proc. Imp. Acad. Tokyo*, 1928, **4**, 271, 275, 354, 471; *A.*, 124.

thinnest films which can be prepared, whereas the scattered X-radiation from such films cannot be detected. There is thus a large special field open to electron analysis. Thin films of all kinds—of oxides [44] formed by corrosion of metals, of animal and plant fibres, of adsorbed gases,[39] and of fats on the surface of liquids—are suitable subjects for examination by the method. Finally, the heating properties of electron beams make them ideal for investigating changes of structure at high temperatures.

The Raman Effect in Crystals.

The Raman effect was discovered, like so many other new phenomena, by tracing to its origin a small and apparently insignificant fact. As early as 1922, Sir C. V. Raman [45] and his co-workers had found what they called a " trace of fluorescence " in a number of liquids when strongly illuminated. It was natural to suppose that this was due to a small amount of impurity, but very careful purification failed to make the " fluorescence " disappear. The phenomenon could not be a true fluorescence, however, because nearly all of a great variety of very pure liquids showed the effect. In 1928 its true nature was revealed by spectroscopic examination. Monochromatic illumination gives rise to scattered light, and in the spectroscope there appears a strong line of unaltered frequency bordered on each side by a number of faint lines. Similar sets of lines appear whatever the wave-length of the incident light, and this, as well as the occurrence of lines on the short wave-length side of the unmodified line, proves that this is a new phenomenon. The differences in frequency between the modified and the unmodified lines of each substance were found to approximate to the frequencies of its infra-red absorption bands. At first it was thought that theory required these frequency-shifts to be exactly equal to the frequencies of the absorption bands, but subsequent work [46] has shown that it is not so. The frequency-shifts of the modified lines are equal to differences between any two characteristic frequencies of the molecule, one of which must be an absorption frequency. The close correlation existing between the Raman effect and molecular vibrations makes this effect of great importance to chemistry and physics. It can show what molecular groups exist in certain compounds and in what way they are modified by their environment; it is equally applicable to all states of matter.

In crystals we have a good medium for investigating, by means of

    [44] M. Ponte, Compt. rend., 1929, 118, 244; A., 367.
    [45] Indian J. Physics, 1928, 2, 387, 399; A., 1928, 685, 1075.
    [46] R. M. Langer, Nature, 1929, 123, 345; A., 379; G. H. Dieke, ibid., p. 564; A., 490; C. P. Snow, Phil. Mag., 1929, [vii], 8, 369; A., 1216.

the Raman effect, the characteristic modes of molecular vibration, for all similar molecules are oriented in the same direction. Much work has been done on the Raman effect in quartz,[47, 48, 49, 50, 51, 52] and the observed frequency-shifts correspond to wave-lengths in the infra-red of 77, 48, 37·5, 28, 24·8, 21·4, 14·3, 12·6, 9·41, and 8·6μ. These should be compared with the infra-red absorption bands, viz., 78, 38, 26·0, 20·75, 12·5, 9·02, and 8·50μ. The correspondence between these sets of figures, although striking, is misleading, because the intensities of corresponding lines are not at all alike. Thus, in the Raman spectra the strongest lines correspond with 77, 48, and 21·4μ, whilst in the absorption spectra the strongest are 8·5, 9·02, 12·5, and 20·75μ, 48μ being entirely absent.[50] We should expect the light scattered from a crystal to be polarised on account of the regular orientation of the molecules. This has been found by Cabannes,[54] who shows that the 21·4 and 48μ radiations are almost completely polarised perpendicular to the incident and scattered light, and 37·5μ parallel to the incident light. This state of polarisation is the same whether the axis of the crystal is parallel to or perpendicular to the incident light. Complicated polarisation effects have also been observed in calcite.[53]

In calcite there also exists a well-defined Raman spectrum [47, 49, 50, 53, 54] having frequency-shifts corresponding with 63·8, 35·3, 14·1, 11·4, 9·24, 6·99, and 5·70μ. The infra-red absorption bands occur at 94, 55, 30, 28, 14·0, 11·4, 7·0, and 6·7μ. The differences in the intensities of the two sets are again remarkable : 9·24μ is a strong line in the Raman spectrum and is absent in the absorption spectra, as it corresponds to an inactive frequency. The absorption frequencies of calcite have been identified with the vibrations of the atoms within the CO_3 group and of this group as a whole in the crystal lattice. The occurrence in the Raman spectrum of the frequency which is inactive in the absorption spectum [55] is an example of the way in which it will be possible greatly to enlarge our

[47] G. Landsberg and L. Mandelstam, Z. Physik, 1928, **50**, 769; A., 9; R. W. Wood, Phil. Mag., 1928, **6**, 729; A., 1928, 1306; H. Nisi, Proc. Imp. Acad. Tokyo, 1929, **5**, 127; A., 742.

[48] P. Pringsheim and B. Rosen, Z. Physik, 1928, **50**, 741; A., 1928, 1307.

[49] I. R. Rão, Indian J. Physics, 1928, **3**, 123; A., 1928, 1306.

[50] K. S. Krishnan, Nature, 1928, **122**, 506; Indian J. Physics, 1929, **4**, 131; A., 1216.

[51] M. Czerny, Z. Physik, 1929, **53**, 317; A., 378.

[52] J. Cabannes, Compt. rend., 1929, **188**, 249; A., 378.

[53] Idem, ibid., p. 1041; A., 627.

[54] M. Kimura and Y. Uchida, Japan. J. Physics, 1928, **5**, 97; A., 241; Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **11**, 199; A., 1216.

[55] C. Schaefer, C. Bormuth, and F. Matossi, Z. Physik, 1926, **39**, 648; A., 1927, 5.

knowledge of the states of excitation of ionic groups. The way in which chemical substitution affects the vibrations of the group is illustrated by a comparison of the Raman lines for $CaCO_3$, *viz.*, 6·9, 9·18, 13·95μ, with those of $NaNO_3$, *viz.*, 7·17, 9·30, 13·7μ.[56] It appears from the two lower wave-lengths that a loosening of the bond between the components of the radical has occurred in the NO_3 group, but for the higher wave-length a tightening has taken place.

Gypsum [50, 56, 57] affords an interesting example of the way in which ionic groups retain their identity in a crystalline environment. There are four prominent lines in the Raman spectrum, at 9·9, 8·81, 2·94, and 2·86μ. The first two can be shown to be due to the SO_4 radical, and the last two to the molecules of water of crystallisation. In aqueous sulphate solutions a line [58] is always obtained at 10·2μ, and it is thought that the two at 9·9 and 8·81 in gypsum are derived from it, the change and splitting being produced by the insertion of the sulphate ion into the crystal lattice. The lines at about 3μ correspond with those given by water itself and by ice,[49] and it seems justifiable to expect that we may always detect in this way the presence of water of crystallisation as distinct from water of constitution in a crystalline substance.

Crystal Chemistry.

The remaining part of the report can now more properly be called Crystal Chemistry than Crystal Structure, for increasing emphasis is being laid on the chemical significance of the structures revealed by X-rays rather than on the structures themselves. Sufficient work has now been done to make possible a systematic classification of solid substances, which expresses at the same time the structure and the chemical and physical properties. The classification first outlined by Grimm [59] and Fajans happily follows in great part that adopted by mineralogists, with the addition of organic substances as a separate group. The four chief divisions are metallic, metalloidal or adamantine, ionic, and molecular, but these groups are not sharply defined and pass insensibly into one another. An example of how the compounds of the element carbon are divided into all four groups is given by A. von Antropoff; [60] Fe_3C metallic, SiC adamantine, Na_4C ionic, and CH_4 molecular; and this classification is used in the

[56] C. Schaefer, F. Matossi, and H. Aderhold, *Physikal. Z.*, 1929, **30**, 581; *A.*, 1216.

[57] R. G. Dickinson and R. T. Dillon, *Proc. Nat. Acad. Sci.*, 1929, **15**, 695; *A.*, 1216.

[58] S. K. Mukherjee and P. N. Sengupta, *Indian J. Physics*, 1929, **3**, 503; *A.*, 976.

[59] Geiger and Scheel, " Handbuch von Theoretischer Physik," Vol. 24.

[60] *Z. Elektrochem.*, 1928, **34**, 113.

following discussion. It will be seen that this arrangement differs from that in previous Reports only in the position of the metals and in the absence of a separate class for elements. Elements, in fact, do not either chemically or physically form a natural division : the majority are metallic and the remainder metalloidal or molecular.

Metallic Crystals.—Our knowledge of the metallic state is more unsatisfactory from the theoretical standpoint than that of any of the other groups. The physical meaning of the forces binding metallic atoms together is still obscure, and the chemical laws regulating the formation of intermetallic compounds are still unknown in the main, although their foundations have been laid by the work of A. Westgren and G. Phragmén, A. J. Bradley, and W. Hume-Rothery described in the last Report.[61] A review of the present state of this subject has been made by J. D. Bernal.[62] A classification of the metallic elements according to their atomic volumes and their places in the periodic system is proposed, and upon this together with considerations of crystal structure, there is based a classification of intermetallic compounds as metallic ionic, metallic homopolar, and purely metallic, depending upon the presence or absence of ions and covalent linkages in the structure. The relation between these and the physical properties (particularly electrical and magnetic) of the metals is discussed. A suggested explanation of the Hume-Rothery rules [61] fixing the ratio of the number of valency electrons to atoms in a structure as $3/2$, $7/4$, or $21/13$, is that they are due to covalent linkages, and this is supported by the fact that most of the compounds obeying the rules have a diamagnetism much too large to be accounted for by single atoms.

The question as to how far Vegard's rule for the lattice dimensions of mixed crystals holds in intermetallic systems, and how far Goldschmidt is justified in using it in deducing atomic radii in metals in the way described in last year's Report, is discussed by A. F. Westgren and G. Phragmén.[63] By measurements of series with similar crystal structure, *e.g.*, Cu–Al, Ag–Al, Ni–Al, they find in every case considerable contraction from what would be expected according to Vegard's rule ; the same is true in the system Cu–Zn, Ag–Zn, Ag–Cd, Cu–Mg, and Fe–W, where compounds exist, and hence it is concluded that Vegard's rule only holds where the component metals are closely related, such as Cu–Au or Mo–W. The constancy of an atomic volume in mixtures must be considered only as a first approximation, there being an almost universal tendency for it to be lower than in the pure elements.

[61] *Ann. Reports*, 1928, **25**, 298 *et seq.*

[62] *Trans. Faraday Soc.*, 1929, **25**, 367 ; *A.*, 987.

[63] *Ibid.*, p. 379 ; *A.*, 987 ; A. Westgren and A. Almin, *Z. physikal. Chem.*, 1929, [*B*], **5**, 14.

V. M. Goldschmidt [64] has determined the crystal structure of rhenium; it is hexagonal close-packed, $a = 2 \cdot 752 \pm 0 \cdot 001$, $c = 4 \cdot 448 \pm 0 \cdot 002$ Å., and resembles that of osmium. The atomic radius is $1 \cdot 371$ Å., which is nearly a mean between those of tungsten and osmium, viz., $1 \cdot 41$ and $1 \cdot 34$ Å., respectively. The density is 21 4. These results are an illustration of the delicacy of X-ray methods in dealing with extremely minute quantities of material.

The structure of strontium as face-centred cubic is confirmed by A. J. King, [65] F. Simon and V. E. Vohsen, [66] and F. Ebert and H. Hartmann [67]; $a = 6 \cdot 075$ Å. at room temperature and $6 \cdot 05$ at the temperature of liquid air. Barium [68] has a body-centred lattice, $a = 5 \cdot 01$ Å. The atomic radii are Sr $2 \cdot 135$, Ba $2 \cdot 17$ Å.

M. Wolf [69] and H. Terrey and C. M. Wright [70] have re-investigated the structure of solid mercury and confirmed the results of L. W. McKeehan and P. P. Cioffi. [71] The structure is rhombohedral-pseudocubic, $a = 4 \cdot 60$ Å., $\alpha = 98° 14'$, being a slight distortion of cubic close packing.

The high-temperature form of manganese has been found by E. Persson and E. Öhman [72] to be the so-called γ- or electrolytic manganese, first studied by Westgren and Phragmén. It is tetragonal, $a = 3 \cdot 77$, $c = 3 \cdot 52$ Å., with a face-centred structure. The pure metal has not been examined in this phase, which is only stable above 1191°, but its existence is verified by extrapolation from a number of manganese alloys in which this phase is stable at lower temperatures. The Cu–Mn alloys form a continuous series of solid solutions varying from the cubic Cu, $a = 3 \cdot 61$ Å., to the tetragonal γ Mn. The conclusions are confirmed by thermal analysis [73] and by the study of the system Mn–N (see p. 292).

A. Pabst [74] has investigated the structures of the gold amalgams. Up to 15% of mercury a normal solid solution is formed. The next phase is a hexagonal close-packed structure approximating to the composition Au_3Hg. At higher mercury contents, two more phases with complicated structures were found.

E. Persson [75] has made a thorough study of the system Cu–Mn–Al

[64] Z. physikal. Chem., 1929, [B], 2, 244; A., 493.
[65] Proc. Nat. Acad. Sci., 1929, 15, 337; A., 749.
[66] Ibid., p. 695; A., 1221.
[67] Z. anorg. Chem., 1929, 179, 418; A., 631.
[68] A. J. King and G. L. Clark, J. Amer. Chem. Soc., 1929, 51, 1709; A., 869.
[69] Z. Physik, 1929, 53, 72; A., 382.
[70] Phil. Mag., 1928, [vii], 6, 1055; A., 16.
[71] Physical Rev., 1922, 19, 444; A., 1923, ii, 864.
[72] Nature, 1929, 124, 333.
[73] (Miss) M. Gayler, J. Iron Steel Inst., 1927, 115, 393.
[74] Z. physikal. Chem., 1929, [B], 3, 443; A., 987.
[75] Z. Physik, 1929, 57, 115; A., 1132.

to find the conditions under which the ferromagnetic Heusler alloys are produced. He concludes that they are due to the definite compound Cu_2MnAl, which exists in annealed specimens. Both the manganese and the aluminium atoms seem to be placed on a face-centred lattice, but there are two alternative positions for the copper atoms, the whole structure being a variant of the body-centred cubic structure with a double cell side. This is in agreement with the work of H. H. Potter,[76] who used single crystals.

In the quenched alloys this double structure is not observed, but the maximum of magnetism is found with alloys having the same composition as that of the compound Cu_2MnAl. S. Valentiner and G. Becker [77] conclude from this that the magnetic properties cannot be due to any particular arrangement of the copper and manganese atoms, but this does not necessarily follow, for it is possible that the arrangement is statistically similar to that of the true compound.

Interstitial compounds. The past year has been notable for studies on a very important set of metallic compounds, *viz.*, those of the transitional elements Cr, Mn, Fe, etc., with the elements of the first series, B, C, N. These compounds are alike in that the lighter element does not replace the metallic one, but enters the gaps in the lattice without altering the size to any great extent. Definite compounds are formed as well as solid solutions. The properties of these alloys are of the greatest importance because essentially they are the basis of the utility of steel. The nitrides have been most studied. The iron–nitrogen system has been examined by G. Hägg,[78] R. Brill,[79] and A. Osawa and S. Iwaizumi,[80] who are all in substantial agreement. The compounds are prepared in all cases by passing ammonia over heated iron, but their properties seem to depend only on their nitrogen content and are independent of the temperature and other conditions of preparation. Apart from a very slight solid solution of nitrogen in iron, two compounds, Fe_4N and Fe_2N, are found. The first is cubic, $a = 3.86$ Å., each cell containing four atoms of iron in a face-centred arrangement (compare γ-iron, $a = 3.63$ Å.) and one nitrogen atom, probably in the centre of the cell surrounded by six iron atoms. Fe_2N, according to Hägg, is orthorhombic pseudo-hexagonal, $a = 2.76$, $b = 4.82$, $c = 4.42$ Å., the iron atoms being in a hexagonal close-packed arrangement, but the position of the nitrogen atoms is uncertain. Osawa has not found the ortho-

[76] *Proc. Physical Soc.*, 1929, **41**, 135; *A.*, 494.

[77] *Z. Physik*, 1929, **57**, 283; *A.*, 1220.

[78] *Nature*, 1928, **121**, 826; **122**, 314, 962; *A.*, 1928, 605, 1081; 1929, 124; *Nov. Act. Reg. Soc. Upsala*, [iv], **7**, No. 1.

[79] *Z. Krist.*, 1928, **68**, 379; *A.*, 748.

[80] *Ibid.*, **69**, 26; *A.*, 1220; *Sci. Rep. Tôhoku Imp. Univ.*, 1929, **18**, 79; *A.*, 986.

rhombic lattice, but, as the variation from the hexagonal is very small, this is not surprising. An intermediate phase containing 8—11% of nitrogen has been found only by Hägg : it is hexagonal close-packed and differs very little from Fe_2N. It has so far been found impossible to produce cobalt or nickel nitrides by the ammonia process, but L. R. Ingersoll and J. D. Hanawalt [81] have produced a tetragonal nickel nitride by sputtering the metal in nitrogen. Hägg [82] has also investigated the system Mn–N. Four phases are found : the first seems to be a solid solution of nitrogen in the tetragonal γ-manganese (see p. 290) and is only stable above 500° ; the next, stable below 400°, is probably Mn_4N and is closely similar to Fe_4N, manganese atoms being on a face-centred cubic lattice, $a = 3\cdot855$—$3\cdot86$ Å. ; the third is similar to the hexagonal Fe_2N with a variable composition (N = 9—12%) ; and the fourth, with 14% of nitrogen, is face-centred tetragonal, pseudo-cubic, $a = 4\cdot19$, $c = 4\cdot03$ Å.

R. Blix [83] has investigated the Cr–N system. The first phase appearing is the hexagonal Cr_2N, but in this case there is a second phase, Cr–N, with the rock-salt structure, isomorphous with the nitrides of V, Ti, Sc, Zr, and Nb. Thus the whole range of elements from scandium to cobalt show a gradation of behaviour towards nitrogen. All these nitrides have the common property of metallic conductivity.

The tetragonal structure in quenched steels mentioned in the last report has now been thoroughly studied by S. Sekito,[84] G. Kurd-jumov, and E. Kaminsky [85] and N. Seljakof.[86] The existence of a tetragonal lattice containing interstitial carbon is confirmed, but the most interesting result is that the axial ratio, particularly the c axial length, increases with the carbon content, the structure being identical with that of α-iron for zero carbon content. In a quenched steel the axial ratio, and consequently the carbon content, in the lattice diminishes steadily from the surface inwards, the rate depending on the velocity of cooling. The hardness of the steel seems also to be a function of the carbon content of this tetragonal phase. On being annealed, it breaks down even at such a low temperature as 100°. At higher temperatures the austenite (γ-iron) disappears and an α-iron–cementite (Fe_3C) mixture is formed.

T. Bjurström and H. Arnfelt [87] examined the Fe–B system and

[81] *Physical Rev.*, 1929, **34**, 972; *A.*, 1368.

[82] *Z. physikal. Chem.*, 1929, [*B*], **4**, 346; *A.*, 1221.

[83] *Ibid.*, 1929, [*B*], **3**, 229; *A.*, 747.

[84] *Sci. Rep. Tôhoku Imp. Univ.*, 1929, **18**, 69; *A.*, 986.

[85] *Z. Physik*, 1929, **53**, 696; **55**, 187.

[86] *Nature*, 1929, **123**, 204; *A.*, 245.

[87] *Z. physikal. Chem.*, 1929, [*B*], **4**, 469; *A.*, 1138.

found two phases: Fe_2B with a body-centred tetragonal lattice, $a = 5.10$, $c = 4.24$ Å., and FeB with an orthorhombic lattice.

Some interesting consequences of the effect of small quantities of the light elements on the polymorphism of iron are suggested by T. D. Yensen.[88] As F. Wever [89] has pointed out, the addition of small quantities of other elements tends either to make the γ- (face-centred) iron disappear in the phase system or to make it the stable form at all temperatures. In particular, silicon tends to make γ-iron disappear, and carbon and oxygen to make it stable. Iron is practically never free from the latter elements. By extrapolation, Yensen finds that the amount of silicon required to prevent the $\alpha \longrightarrow \gamma$ change in iron would be vanishingly small in the absence of carbon and oxygen; consequently, absolutely pure iron would show no allotropic forms and would remain body-centred at all temperatures. It would be very interesting to see whether such iron could be produced experimentally.

So far the only interstitial compound of hydrogen known with certainty is Pd_2H. From the work of J. D. Hanawalt [90] the existence of such a compound seems to be proved, although its composition is somewhat variable. It is face-centred cubic, $a = 4.017$, as against 3.873 Å. for pure palladium. Nickel and platinum may form similar compounds but the evidence so far is conflicting.[91]

Adamantine Compounds.—There is some difficulty in finding a suitable name for this class of compound. Chemically, it consists mostly of compounds of the transition metals with the lower elements of Groups IV, V, and VI, so that sulphides would seem to be too narrow a term and metalloidal too vague. The compounds are characterised by a binding of a homopolar nature throughout the crystal, but the use of the term " homopolar " might give rise to confusion with organic crystals. " Adamantine " is chosen because the greater number of them actually have the diamond structure or a variant of it, and the diamond is the most perfect example of this kind of binding in crystals. Of the sulphides, covelline has been studied by H. S. Roberts and C. J. Ksanda [92]; the natural mineral is identical with CuS (prepared either by precipitation or by direct synthesis), it is hexagonal, $a = 3.80$, $c = 16.43$ Å., in agreement with the results of B. Gossner and F. Mussgnug,[93] and contains 6 copper

[88] *Science*, 1928, **68**, 376; *A.*, 1135.

[89] *Naturwiss.*, 1929, **17**, 304; *A.*, 745.

[90] *Physical Rev.*, 1929, [ii], **33**, 444.

[91] R. Salvia, *Anal. Fís. Quím.*, 1929, **27**, 285; *A.*, 870; S. Valentiner and G. Becker, *Naturwiss.*, 1929, **17**, 639; *A.*, 1130; L. R. Ingersoll and J. D. Hanawalt, *Physical Rev.*, 1929, **34**, 972; *A.*, 1368.

[92] *Amer. J. Sci.*, 1929, [v], **17**, 489; *A.*, 870.

[93] *Centr. Min.*, 1927, [*A*], 410.

and 6 sulphur atoms. The space group is D_{6h}^4 and a structure is proposed, but the X-ray data are not sufficient to verify it. L. Thomassen [94] has examined the binary compounds of the platinum metals with the elements of Groups V and VI. Nine compounds, $OsTe_2$, $OsSe_2$, $RuTe_2$, $RuSe_2$, RuS_2, PtP_2, $PtAs_2$, $PtSb_2$, and $PdAs_2$ have the pyrites structure; four, $PdTe_2$, $PtTe_2$, $PtSe_2$, and PtS_2, have the cadmium iodide structure; and two, $PdSb$ and $PdTe$, have the nickel arsenide structure. It was thought that, from analogy with iron compounds, some of these new compounds might be ferromagnetic, but this is not so. G. Hägg [95] has investigated the binary systems of iron with P, As, Sb, and Bi, but they do not offer many analogies; Fe_3P has a tetragonal body-centred cell, space group S_4^2; Fe_2P is hexagonal; FeP may exist, but its structure is complicated. Fe_2As is tetragonal, $a = 3\cdot63$, $c = 5\cdot97$ Å., the cell containing two molecules, and the arsenic atoms apparently being arranged on tetragonal axes between two iron atoms; $FeAs$ is orthorhombic with a distorted nickel arsenide structure. $FeSb$ has the latter structure but is of variable composition. $FeSb_2$ has the space group Q_h^{12} and is apparently isomorphous with marcasite, FeS_2, and löllingite, $FeAs_2$, studied by Frielinghaus [96] and W. F. De Jong.[97]

A. Westgren, G. Hägg, and S. Eriksson [98] have investigated the Cu–Sb and Ag–Sb systems. In the former, there are three phases : solid solution, a hexagonal close-packed phase of composition varying from 19 to 25% of Sb (roughly corresponding with the compound Cu_3Sb), and a definite compound Cu_2Sb with a tetragonal structure apparently isomorphous with Fe_2As (see above). In the Ag–Sb system a hexagonal close-packed phase was also found corresponding roughly to Ag_3Sb, but the remaining phase (from 20 to 25% of Sb, of variable composition) is orthorhombic pseudo-hexagonal.

The phosphides and arsenides of some bivalent metals have been studied by L. Passerini [99] : Zn_3P_2, Cd_3P_2, Mg_3P_2, Zn_3As_2, and Cd_3As_2 are all isomorphous and belong to a new structure type with a cubic cell $a \approx 6$ Å., containing six metal atoms in the centre of the faces and of the edges of the cube and 4 arsenic or phosphorus atoms in the centres of alternate octants ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$). The structure has a certain analogy to that of zinc blende.

The more complicated adamantine compounds have been very little investigated, but F. Machatschki [1] has examined the structure of a great number of tetrahedrides which are complicated antimony

[94] Z. physikal. Chem., 1929, [B], 2, 349 ; [B], 4, 277 ; A., 1221.
[95] Z. Krist., 1928, 68, 470 ; A., 749 ; see also refs. (78).
[96] Diss., Greifswald, 1926.   [97] Physica, 1926, 6, 325.
[98] Z. physikal. Chem., 1929, [B], 4, 453 ; A., 1139.
[99] Gazzetta, 1928, 58, 655, 775 ; A., 125, 246.
[1] Z. Krist., 1928, 68, 204 ; A., 747.

sulphides of the general formula R_3SbS_3 ($R = Cu$, Ag, etc., or Fe, Zn, Pb, etc.). The unit cell is cubic, $a = 10\cdot3$ Å., and contains component cells very similar to zinc blende, $a = 5\cdot42$ Å. The exact positions of the atoms are somewhat uncertain owing to the variable composition. Another similar compound, sulvanite, Cu_3VS_4, has been studied by de Jong [2]; it is also cubic, $a = 10\cdot75$ Å.

Ionic Compounds.—The most important contribution made to the study of ionic crystal structures is that of L. Pauling [3] on " The Principles Determining the Structures of Complex Ionic Crystals." Here the ideas of Goldschmidt on the importance of ionic size and the results of W. L. Bragg's silicate investigations are systematised and extended into a set of rules which give the possible structures for ionic compounds composed of a number of positive and negative ions of different sizes. The rules do not apply where the ions are very large or where homopolar bonds are found, but they nevertheless cover the greater part of inorganic crystals. The guiding principle is that the geometrical nature of a structure is primarily determined by the anions which may be considered as forming co-ordination polyhedra around the smaller kations. This idea had already been used extensively by Bragg and Goldschmidt, but Pauling has made the important addition that, not only the arrangement of anions round each kation, but also that of kations round each anion must be considered; in general terms, the stability of a structure is assured only when the charge induced by neighbouring kations on an anion is equal and opposite to its own charge. The five rules are as follows :

(1) " A co-ordinated polyhedron of anions is formed about each kation, the kation–anion distance being determined by the radius sum and the co-ordination number of the kation by the radius ratio." As in the great majority of cases the anions are O″ or F′ ions of radius $1\cdot33$ Å., the co-ordination depends only on the kation. The number is 3 (triangle) for B^{III}; 4 (tetrahedron) for (B^{III}), $Be^{\cdot\cdot}$, $Li^{\cdot}$, Si^{IV}, (Al^{III}); 6 (octahedron) for Al^{III}, $Mg^{\cdot\cdot}$, Ti^{IV}, Sc^{III}, Mo^{VI}, Nb^{V}, Zr^{IV}. Where the co-ordination is greater than 6, as with large kations, the great distortion of the polyhedron renders the rule inapplicable.

(2) " In a stable co-ordination structure the electric charge of each ion tends to compensate the strength of the electrostatic valence bonds reaching it from the kations at the centres of the polyhedra at which it forms a corner; that is, for each anion $\zeta = \Sigma_i z_i/\nu_i$", where ζ is the charge of the anion, z_i the charge of the kation, and ν_i the number of anions surrounding each kation, the

[2] *Z. Krist.*, 1928, **68**, 522; *A.*, 988.

[3] *J. Amer. Chem. Soc.*, 1929, **51**, 1010; *A.*, 748.

sum being taken for all kations whose polyhedra have this anion as their common corner. For example, in topaz each oxygen ion is common to one silicon tetrahedron and two aluminium octahedra. Consequently, $\Sigma z/\nu = \frac{4}{4} + \frac{3}{6} + \frac{3}{6} = 2$, whereas each fluorine ion is common to 2 aluminium octahedra, and $\Sigma z/\nu = \frac{3}{6} + \frac{3}{6} = 1$.

(3) " The presence of shared edges and particularly of shared faces in a co-ordinated structure decreases its stability. This effect is large for kations with large valence and small co-ordination number and is especially large in case the radius ratio approaches the lower limit of stability of the polyhedron." The truth of this rule depends on the Coulomb repulsion of neighbouring kations, which is naturally larger when an edge of two polyhedra is shared than when a corner is shared, and still larger when a face is shared. Consequently, silicon tetrahedra tend to share only corners with other polyhedra. Titanium octahedra share only corners and edges, whilst aluminium octahedra sometimes, as in corundum, share faces.

(4) " In a crystal containing different kations, those with large valence and large co-ordination number tend not to share polyhedron elements with each other." Consequently, silicon tetrahedra share no elements with each other if the oxygen–silicon ratio is equal to or greater than 4, e.g., topaz, zircon, olivine, and orthosilicates in general. This gives an important method of classification for silicates.

(5) " The number of essentially different kinds of constituents in a crystal tends to be small." This rule is of a much more doubtful character than the others. It is certain that in a number of purely geometrical possibilities the actual one in nature will probably not be the most complicated, but it would seem unsafe to go further.

The rules are supplemented by consideration of how the polyhedra built together in this fashion are liable to be distorted by their mutual forces. To do this completely would require a solution of the equation of state of the crystal to find the minimum crystal energy, but empirical rules have a wide range of validity. Polyhedra of oxygen ions about tervalent and quadrivalent kations are distorted in such a way as to shorten shared edges and edges bounding shared faces to 2·50 Å. instead of 2·7 Å. These rules, which are admittedly only a rough first approximation, have nevertheless already proved extremely valuable for the accurate prediction of crystal structures to be checked by X-rays, or for the selection of structurally plausible crystal structures when the X-ray data are ambiguous or insufficient. An example of the first use is afforded by the case of brookite and topaz discussed in last year's Report.[4] The second is exemplified by the cases of cyanite (see below, p. 299),

[4] *Ann. Reports,* 1928, **25**, 285, 286.

of the chlorides of the bivalent metals,[5] and of the A class of the sesquioxides of the rare-earth metals.[6] From the measurements of G. Bruni and A. Ferrari,[7] Pauling has calculated the probable structure of the chlorides of Cd, Mg, Ni, Co, Mn, Zn, Ru, Rh, Pd, Ir, and Pt. Each metal atom is surrounded by six chlorine atoms at the corners of a regular octahedron which shares six edges with neighbouring octahedra to form a double layer of chlorine atoms with the metal atoms between. Three of these layers, attached together by the residual attraction of the metals, go to build up the rhombohedral cell. This structure seems to be stable for compounds of the type AX_2, where A has a co-ordination number 6 and X is not too polarisable, in which case there is a transition to the cadmium iodide class. In the case of the A type of the sesquioxides, *i.e.*, those of La, Ce, Pr, and Nd, Pauling has proposed a similar layer structure of shared octahedra instead of that proposed by W. H. Zachariasen.[8] A further example of the application of Pauling's principles is shown in his theory of the silicotungstic acids (see p. 301).

We may divide ionic crystals into three main groups : (1) simple oxides and halides of the type $A_n X_m$, (2) complex oxides, including silicates, of the general type $A_n B_p \ldots \ldots X_m$, not containing separate complex ions of the type AX_n, and (3) complex ionic compounds and co-ordination compounds.

A number of new structural types have been found among simple compounds. I. Oftedal[9] has studied the trifluorides of the rare-earth metals La, Ce, Pr, Ne, and Sa, which are isomorphous with the natural mineral tysonite. The structure is hexagonal, $a \approx 7 \cdot 1$, $c \approx 7 \cdot 3$ Å., containing 6 molecules RF_3. The space group is D_6^4. The metal atoms form a hexagonal close-packed assembly, but the position of the fluorine atoms, owing to their very small scattering power, is still doubtful. O. Hassel and S. Nilssen[10] have determined the structure of bismuth fluoride. It is cubic, $a = 5 \cdot 85$ Å., with 4 molecules in the cell; the bismuth atoms form a face-centred cubic structure with the fluorine atoms probably on the cell edges and in the centres of the octants, each bismuth atom being thus surrounded by 14 flourine atoms. The crystal structures of the fluorides of the metals of Group VIII have been studied by O. Ruff and E. Ascher[11] : FeF_2, CoF_2, NiF_2, and PdF_2 have the rutile

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[5] *Proc. Nat. Acad. Sci.*, 1929, **15**, 709; *A.*, 1221.

[6] *Z. Krist.*, 1929, **69**, 415; *A.*, 1223.

[7] *Atti R. Accad. Lincei*, 1926, [vi], **4**, 10; *A.*, 1926, 995.

[8] *Z. physikal. Chem.*, 1926, **123**, 134; *A.*, 1926, 1195; *Z. Krist.*, 1929, **70**, 187.

[9] *Z. physikal. Chem.*, 1929, [*B*], **5**, 272; *A.*, 1223.

[10] *Z. anorg. Chem.*, 1929, **181**, 172; *A.*, 987.   [11] *Ibid.*, 1929, **183**, 193.

structure, and there are two new types—those of FeF_3 and CoF_3, which are hexagonal, and of RhF_3 and PdF_3, which are orthorhombic. The full X-ray data, however, have not yet been published. H. Bräkken and L. Harang [12] have determined the structure of $PbCl_2$, $PbBr_2$, and $HgCl_2$. The first two are isomorphous, and all have the same space group Q_h^{16}. All the atoms lie in symmetry planes and the structure is probably molecular. The existence of similar molecules of PbCl has been suggested by the study of the chlorocarbonates of lead by M. Matthieu and (Mme.) N. Demassieux.[13]

Italian and other workers [14] have made an extensive study of isomorphism of the compounds of the bivalent metals Zn, Ni, Mg, Co, Fe, Mn, Cd, and Ca, whose atomic radii range from 0·75 to 1·08 Å. Fluorides, chlorides, oxides, hydroxides, carbonates, and sulphides have been studied by X-ray methods, both singly and in mixed crystals. Except for extreme members, such as Ca and Zn, complete miscibility in the solid state is found for most compounds, and it appears from these studies that the only relevant factor for isomorphism is ionic size. A point of some interest is the formation of mixed crystals of hydroxide by precipitation from solutions of the mixed chlorides.

Of complex oxides, apart from silicates, the spinels have been most studied in the past year. S. Holgersson [15] has prepared and examined 17 of these, all isomorphous and with cell size varying from 8·04 Å. for $CuAl_2O_4$ to 8·57 Å. for $MnFe_2O_4$. Spinels have been made with nearly every one of the bivalent metals Cu, Zn, Ni, Mg, Co, Fe, Mn, Cd, and the tervalent metals Al, Cr, Fe. Other interesting spinels are those of cobalt, including tricobaltic tetroxide [16] and the pigments $ZnCo_2O_4$ and $SnCo_2O_4$.[17] J. Böhm [18] has made a thorough study of the natural and artificial hydrated iron oxides, which appear to be mixtures of anhydrous oxides with various proportions of semi-hydroxide $FeO(OH)$, which exists in an α- and a γ-form : only

[12] Z. Krist., 1928, 68, 123; A., 631.

[13] Compt. rend., 1929, 189, 333, 536; A., 1154, 1252.

[14] G. Natta, Gazzetta, 1928, 58, 344, 419; G. Natta and L. Passerini, ibid., pp. 541, 597; 1929, 59, 129; L. Passerini, ibid., p. 144; A., 639; A. Ferrari, A. Celeri, and F. Giorgi, Atti R. Accad. Lincei, 1929, [vi], 9, 782; A., 996; S. Holgersson and A. Karlsson, Z. anorg. Chem., 1929, 182, 255; A., 1130.

[15] Lunds Univ. Årsskr., [ii], Avd. 2, 23, 9; Chem.-Zentr., 1929, i, 372; A., 1131.

[16] S. B. Hendricks and W. H. Albrecht, Ber., 1928, 61, [B], 2153; A., 15; G. Natta and L. Passerini, Gazzetta, 1929, 59, 280; A., 870; L. Passerini, Atti R. Accad. Lincei, 1929, [vi], 9, 338; A., 673.

[17] G. Natta and L. Passerini, Gazzetta, 1929, 59, 620.

[18] Z. Krist., 1928, 68, 567; A., 988.

the first is found in natural minerals. Both structures are ortho-rhombic, and the α-form is isomorphous with diaspore, AlO(OH).

Silicates.—The investigation of the main types of silicate structure is nearing completion. Their study has been much simplified by the facts that the mineralogical classification of silicates has proved to be a natural one, and that X-rays have shown all members of such families as felspars, pyroxenes, micas, etc., to have nearly identical structures. A complete survey of the present state of knowledge of the silicate structures, which has been so largely his own work, is given by W. L. Bragg.[19] The great advantage of his method of working was that it rigorously followed the X-ray data so that the positions assigned to the atoms are quite independent of any theories as to the constitution of silicates. Nevertheless, as the work con-tinued, the general plan of building of silicates became apparent, and we are now in a position to predict complicated structures and even to reduce the method of prediction to rules as Pauling has done.[20] Many important silicate types have been completely deter-mined in the past year. C. Menzer [21] has made a very thorough study of the garnet group, the general formula of which is $A_3B_2Si_3O_{12}$, where A is Ca, Fe, Mn, or Mg, and B is Al, Fe, or Cr. The cell is cubic, $a \approx 12$ Å., containing 4 molecules, but the cubic symmetry makes the structure a relatively simple one. Pauling's rules are very well followed : each silicon atom is sur-rounded by 4 oxygen atoms, each aluminium by 6 oxygens, and each calcium by 8 oxygens. All the silicon tetrahedra are separate, and every oxygen atom has as neighbours one aluminium, one silicon, and two calcium atoms. It is a typical ortho-structure in Machat-schki's sense.[22]

The structure of the three forms of aluminium silicate is now fully known. Andalusite has been shown by W. H. Taylor [23] to have a very similar structure to sillimanite, both being based on chains of alumin-ium octahedra bound together by silicon tetrahedra, but having besides a certain number of aluminium atoms—in sillimanite be-tween 4 oxygen and in andalusite between 5 oxygen atoms—so that the formula of these compounds might be written $Al \cdot AlSiO_5$, whereas in cyanite all the aluminium atoms are between 6 oxygen atoms. The structure of cyanite has been altered [24] in regard to the position of the silicon ions, since Pauling had pointed out that these lay too close together in the structure originally proposed.[25]

[19] *Trans. Faraday Soc.*, 1929, **25**, 291; *A.*, 749.
[20] See p. 295.   [21] *Z. Krist.*, 1929, **69**, 300.
[22] See *Ann. Reports*, 1928, **25**, 284.   [23] *Z. Krist.*, 1929, **71**, 205.
[24] S. Náray-Szabó, W. H. Taylor, and W. W. Jackson, *Z. Krist.*, 1929, **71**, 117.
[25] W. H. Taylor and W. W. Jackson, *Proc. Roy. Soc.*, 1928, [*A*], **119**, 132.

The structure of staurolite has close analogy to that of cyanite, as has been pointed out by G. M. Cardoso.[26]   S. Náray-Szabó[26] has completed its analysis and shown it to be essentially composed of layers of cyanite and ferrous hydroxide in very much the same way as in the humite series, so that its formula should be written $2Al_2SiO_5,Fe(OH)_2$. The structure of norbergite, the first of the olivine–clinohumite series, has been determined by W. H. Taylor and J. West[28] : it consists of alternating layers of Mg_2SiO_4 and $Mg(OH)_2$. Norbergite, chondrodite, humite, and clinohumite consist respectively of 1, 2, 3, and 4 layers of olivine separated by one layer of $Mg(OH)_2$.

B. E. Warren[29] has now analysed the structure of tremolite. His results are detailed in the Report on Mineralogical Chemistry (p. 257), but it is noteworthy that the formula now found, which is based on X-ray data, actually agrees better with chemical analysis than the older formula, thus showing the value of X-ray methods for the determination of the constitution of complex substances.

E. Schiebold[30] has shown that the felspars, monoclinic and triclinic, have all very similar structures but the actual structure has not yet been worked out. The relationships between the felspars undoubtedly depend on a substitution of aluminium in silicon–oxygen tetrahedra. Such structures are found in the ultramarines $Na_8Al_6Si_6O_{24}S_x$, on which F. M. Jaeger[31] has continued his researches. The basis of the structure, and of that of the natural minerals nosean and haüyine, is a skeleton of 12 atoms of aluminium and 12 of silicon, all inside oxygen tetrahedra and linked into a cubic structure. The remaining atoms of sodium, sulphur, etc., are placed in the holes of the structure, some in fixed and others in free positions. This existence of a silicon–aluminium skeleton will probably explain all the peculiar properties of zeolitic minerals, in which replacement of atoms can take place without any alteration of structure.

Complex Ionic Compounds.—Compounds of the symmetrical AX_4 ion form a very definite class. The particular nature of the AX_4 ion seems to be almost immaterial. Beryllo-fluorides, sulphates, perchlorates, and permanganates all form isomorphous compounds and mixed crystals.[32]   A particularly interesting study is the system

[26] *Ber. Sächs. Akad. Wiss.*, 1929, **80**, 165; *Centr. Min.*, 1928, [A], **11**, 390.

[27] *Z. Krist.*, 1929, **71**, 103.

[28] *Ibid.*, **70**, 461; see also *Ann. Reports*, 1928, **25**, 284.   [29] *Ibid.*, **72**, 42.

[30] *Trans. Faraday Soc.*, 1929, **25**, 315; *A.*, 749; *Fortschr. Min. Krist. Petr.*, 1927, **12**, 78.

[31] *Trans. Faraday Soc.*, 1929, **25**, 320; *A.*, 749; *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 156, 167.

[32] P. C. Rây, *Nature*, 1929, **124**, 480; *A.*, 1220; W. R. C. Curjel, *ibid.*, 1929, **123**, 206; *A.*, 246.

$BaSO_4$–$KMnO_4$ [33]; here a univalent kation and a univalent anion both replace bivalent ions without any apparent difficulty, isomorphism again seeming to depend only on ionic size. L. Vegard and A. Maurstad [34] have completely determined the structure of the anhydrous alums $KAl(SO_4)_2$, $NaAl(SO_4)_2$, $NH_4Fe(SO_4)_2$, and $KCr(SO_4)_2$. They are hexagonal, space group D_3^2; the sulphate ions have simple trigonal symmetry and are rather similarly arranged to those of $KLiSO_4$. Each aluminium atom is surrounded by 6 and each potassium atom by 12 oxygen atoms. The structure of gypsum, $CaSO_4,2H_2O$, has been determined by E. Onorato.[35] It is a typical layer lattice in which the calcium and sulphate ions lie in the b planes separated by the water molecules. E. Broch [36] has established the form of the monoclinic tungstates of Fe, Mn, Co, Ni, and Mg, and shown that potassium per-rhenate, $KReO_4$, belongs to the scheelite type.

The form of the chlorate ion has been exactly determined by W. H. Zachariasen,[37] who has studied the structure of sodium and potassium chlorates by means of Fourier analysis. This shows without possibility of doubt that the chlorine and oxygen atoms do not lie in a plane, as the carbon and oxygen atoms do in the CO_3'' ion, but form an obtuse pyramid, the oxygen atoms being in a triangle of 2·38 Å. side and the chlorine atom being 0·48 Å. out of [the plane. This arrangement is probably also found in the ions PO_3''', SO_3'', AsO_3''', SeO_3'', and SbO_3'''—in fact, wherever the valency of the central atom is less by 2 than its full valency. The formation of an AX_3 ion out of one of AX_4 is consequently merely the removal of one of the anions without distortion of the rest of the structure. This is in agreement with the suggestion of A. M. Taylor,[38] based on spectral data, that the bonds holding together such ions are of a semipolar and not of an ionic type.

Pauling has extended his ideas on the linking of oxygen polyhedra to the explanation of complex ions of the silicotungstic acids.[39] In his view, the essential basis of the structure is 12 tungsten atoms, each surrounded by 3 oxygen atoms and 3 hydroxyl groups and linked together through the former into a structure resembling a truncated tetrahedron. Inside this tetrahedron is found the characteristic ion, SiO_4 for silicotungstates, BO_4 for borotungstates, etc., thus giving a formula for silicotungstic acid,

$$H_4[SiO_4,W_{12}O_{18}(OH)_{36}].$$
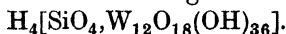
[33] G. Wagner, *Z. physikal. Chem.*, 1929, [B], **2**, 27; *A.*, 247.

[34] *Z. Krist.*, 1929, **69**, 519; *A.*, 1221.   [35] *Ibid.*, **71**, 277.

[36] *Z. physikal. Chem.*, 1928, [B], **1**, 409; 1929, [B], **6**, 22; *A.*, 245.

[37] *Z. Krist.*, 1929, **71**, 501, 517.

[38] *Trans. Faraday Soc.*, 1929, **25**, 314; *A.*, 749.

[39] *J. Amer. Chem. Soc.*, 1929, **51**, 2868; A. G. Scroggie and G. L. Clark, *Proc. Nat. Acad. Sci.*, 1929, **15**, 1; *A.*, 246.

In this way he is able to explain the large number of molecules of water of crystallisation and the basicity of the acids. Similar explanations probably hold for all ions containing large numbers of metallic atoms. O. Hassel and H. Kringstad [40] have continued their work on complex co-ordination compounds, in particular the cobaltammine and chromammine chloratosulphates and perchlorato-sulphates, both in hexammino- and pentamminoaquo-forms. The existence of two kinds of complex anion makes very little difference to the nature of the structures, which are in all cases cubic.

K. Hermann and W. Ilge [41] have studied tetramethylammonium perchlorates and permanganates : the structure is tetragonal. After consideration of possible alternatives, both ions are shown to be tetrahedral. In connexion with such compounds, it should be mentioned that the statements in last year's Report require correction; Vegard's original structure [42] for the iodide only differed from those of other workers in the position of the carbon atoms, and no mention was made of the subsequent paper [43] in which he described the correct structure.

Molecular Crystals.—From the strictly crystallographic point of view, the system of classification for molecular substances should be based on the way in which the separate molecules are bound together to form the crystal. This may vary from van der Waals forces, as in permanent gases and hydrocarbons, to cases where the polarity of the molecules is so strong that the force binding the positive end of one molecule to the negative end of another is as effective as in an ionic crystal such as those of ice, dibasic acids, or sugars. However, insufficient structures have been studied to make this classification possible, and that now to be employed is based on the inner constitution of the molecule, the chief divisions being (1) simple molecular structures, (2) aliphatic, and (3) aromatic compounds.

(1) The structure of solid nitrogen has been studied by L. Vegard [44] and by J. de Smedt and W. H. Keesom.[45] Both find a cubic cell, $a = 5{\cdot}66$ Å., containing four molecules. Vegard considers the structure to be cubic, space group T^4, the distance between two atoms in a molecule being $1{\cdot}06$ Å., and the molecular structure resembling that of argon (face-centred cubic, $a = 5{\cdot}42$ Å.). On the other hand, the other investigators, from identical X-ray data, conclude that the structure is tetragonal on account of the double refraction. Solid nitrogen exists in two forms, one stable below 36° Abs., and the other

[40] *Z. anorg. Chem.*, 1929, **182**, 281; *A.*, 1222.

[41] *Z. Krist.*, 1929, **71**, 47.   [42] *Phil. Mag.*, 1917, [vi], **33**, 395.

[43] *Ibid.*, 1927, [vii], **4**, 985; *A.*, 1928, 7.

[44] *Nature*, 1929, **124**, 267, 337; *Naturwiss.*, 1929, **17**, 543, 672; *A.*, 987, 1130; *Z. Physik*, 1929, **58**, 497.

[45] *Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 745; *A.*, 1130.

between 36—62° Abs. It may be, as in the case of methane, that although the apparent temperature was below 36° Abs., the necessary exposure of the substance for the X-ray examination caused the outer layers to be above the transition temperature, and the cubic structure described really belongs to β-nitrogen, the α-form having double refraction. Alternatively, the double refraction may, as in many similar cases, be due to strain.

An important controversy has been settled in a very thorough study by W. H. Barnes [46] of the structure of ice. Single crystals were used and the temperature ranged from 0° to − 183°. The cell is hexagonal, $a = 4.53$ Å., $c = 7.41$ Å, containing four molecules. The space group is D_{6h}^4. The oxygen atoms can be definitely placed in a wurtzite arrangement, but the position of the hydrogen atoms is still indeterminate, although they are almost certainly placed somewhere between the pairs of oxygen atoms. The structure agrees with that of (Sir) W. H. Bragg [47] and D. M. Dennison.[48] This still leaves open the question as to the chemical nature of ice. Barnes inclines to the view that it is an ionic structure of H· and O″. A molecular structure $H\diagdown^{O}\diagup H$ would seem impossible from the cell and the symmetry, but it must be remembered that, with its small scattering power, a larger cell due to hydrogen alone would probably not be detected, and evidence on other grounds, particularly the Raman effect,[49] favours the existence of water molecules in ice, although these are so strongly polar that the whole structure will obviously resemble an ionic crystal in its physical properties.

(2) J. C. McLennan and W. G. Plummer [50] have determined the structure of methane. The molecules are in a face-centred cubic arrangement, $a = 6.35$ Å., and the space group is either T_2 or T_d^2. The hydrogen atoms cannot be exactly placed but are probably tetrahedrally arranged. No different structure was found above and below the transition temperature, 20° Abs.

The structure of urea has been determined by S. B. Hendricks.[51] The cell is tetragonal, $a = 5.73$, $c = 4.77$ Å., containing 2 molecules, space group D_{2d}^3. The carbon, oxygen, and two nitrogen atoms lie in a plane. The polar axis of the molecule is parallel to the tetragonal axis, and the amine end of one molecule is next to the oxygen in the neighbouring molecule, forming a typical polar molecular structure.

[46] *Proc. Roy. Soc.*, 1929, [*A*], **125**, 670.
[47] *Proc. Physical Soc.*, 1922, **34**, 98.
[48] *Physical Rev.*, 1921, **17**, 20.
[49] I. R. Râo, *Indian J. Physics*, 1928, **3**, 123; *A.*, 1928, 1306.
[50] *Phil. Mag.*, 1929, [vii], **7**, 761; *A.*, 750.
[51] *J. Amer. Chem. Soc.*, 1928, **50**, 2455; *A.*, 1928, 1175.

Thiourea has a similar structure, but of lower, orthorhombic symmetry.

Considerable work has been done on long-chain compounds. A. Müller [52] explains the well-known alternation of properties between compounds with odd and even numbers of carbon atoms as being due to the zigzag character of the chain. When the number of carbon atoms is even, the orientations of the end groups are parallel; when it is odd, they make an angle with each other. This difference affects the placing of the molecules in the next layer, leading to a difference in the inclination of the chain which affects the physical properties. In the dicarboxylic acids studied by W. A. Caspari,[53] this difference results in the c axis of the crystal being doubled in the odd-carbon acids. New measurements on fatty acids and their salts have been made by S. H. Piper [54] and by G. T. Morgan and E. Holmes.[55]

Several further studies have been made on pentaerythritol [56] and its substitution products, but all now agree to a tetrahedral structure of the carbon atom. The most interesting is that of dibenzylidene-pentaerythritol by F. A. van Melle and H. B. J. Shurink.[57] The hexagonal cell contains 3 molecules of the structure
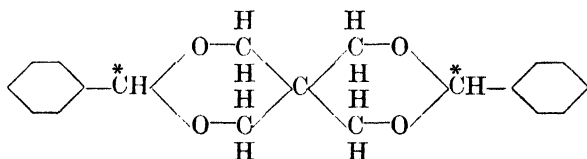
each possessing a diagonal axis along its length. This implies that the substituents of the carbon atoms marked * all lie in a plane. Even if the position of the hydrogen atom is neglected, this is rather a remarkable result and invites further study. A number of measurements have been made by A. Reis and W. Schneider [58] on the cells and space-groups of tartaric and fumaric acids and their salts and other similar substances. I. Nitta [59] has made a similar examination of the rhombic formates.

(3) (Mrs.) K. Lonsdale [60] has now published a full account of the

[52] *Proc. Roy. Soc.*, 1929, [*A*], **124**, 317; *A.*, 869.   [53] *J.*, 1928, 3235.

[54] *J.*, 1929, 234; *Trans. Faraday Soc.*, 1929, **25**, 348; *A.*, 751.

[55] *J. Soc. Chem. Ind.*, 1928, **47**, 309T; *A.*, 245.

[56] E. Ernst, *Z. Krist.*, 1928, **68**, 139; *A.*, 751; (Miss) I. E. Knaggs, *Proc. Roy. Soc.*, 1929, [*A*], **122**, 69; *A.*, 246; H. Möller and A. Reis, *Z. Krist.*, 1928, **68**, 385; *A.*, 988; H. Mark and G. von Susich, *ibid.*, **69**, 105; *A.*, 1223.

[57] *Z. Krist.*, 1928, **69**, 1; *A.*, 1223.

[58] *Ibid.*, **68**, 543, 586; **69**, 49, 62; *A.*, 988, 1223.

[59] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1928, **9**, 151.

[60] *Proc. Roy. Soc.*, 1929, [*A*], **123**, 494; *A.*, 750; *Trans. Faraday Soc.*, 1929, **25**, 352.

structure of hexamethylbenzene, based on exact intensity measurements of a great number of planes, and on an exhaustive consideration of alternative structures. The cell is triclinic, $a = 9.010$, $b = 8.926$, $c = 5.344$ Å., $\alpha = 44° 27'$, $\beta = 116° 43'$, $\gamma = 119° 34'$, but is very pseudo-hexagonal. The benzene rings and the six methyl groups all lie within the c plane or within 0·1 Å. of it. The molecule is nearly hexagonal but actually only possesses a centre of symmetry, and the molecules in successive layers show no particular relation to each other. The diameter of the carbon atom is 1·42 Å. This demonstration would seem to decide the flat character of the benzene ring, but unfortunately it is by no means certain that the nature of the ring does not depend on its substituents. The investigation of naphthalene and anthracene with the object of finding the exact position of the carbon atoms has been made by J. M. Robertson.[61] Here the evidence points equally conclusively to a puckered ring, but as the paper was published in error before completion, fuller comment is deferred.

The study of a very interesting group of aromatic substances has been made by J. Hengstenberg and H. Mark [62]; the structures of diphenyl, phenanthrene, and fluorene are very similar (excepting that in the last two the c axis is doubled), which suggests that the two main benzene rings must be similarly placed in all cases. They have further investigated [63] the series of " polyenes,"

$$C_6H_5 \cdot \dot{C} : \dot{C} \cdot \dot{C} : \dot{C} \cdots C \cdot C_6H_5$$
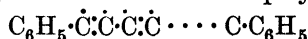
in which double- and single-bonded carbon atoms alternate, and find that the increase in length per pair of double-bonded carbon atoms is 1·5 Å., as against 2·5 Å. in the paraffins, pointing to a chain of the type |_|⎺|_|⎺ rather than a simple zigzag, thus ＼／＼／＼／.

An enormous amount of work has been done in the past year on the structure of cellulose and its derivatives, on rubber, silk, and similar substances, all of which have in common the existence of very long molecules consisting of identical groups bound together by covalent links. It is impossible in the space of this report to comment on this work, and only a few of the most important references are given.[64] Further work has shown that the size of the pseudo-cell of cellulose is probably twice as large as previously believed,

[61] *Proc. Roy. Soc.*, 1929, [A], **125**, 542; *A.*, 1367.

[62] *Z. Krist.*, 1929, **70**, 287.

[63] *Trans. Faraday Soc.*, 1929, **25**, 414.

[64] H. Mark and K. H. Meyer, *Z. physikal. Chem.*, 1929, [B], **2**, 115; **4**, 431; *A.*, 245, 1132; K. R. Andress, *ibid.*, [B], **2**, 380; K. Weissenberg, *Naturwiss.*, 1929, **17**, 181, 624; *A.*, 493; C. Trogus and K. Hess, *Z. physikal. Chem.*, 1929, [B], **4**, 321; [B], **5**, 161; *A.*, 1222; A. Burgeni and O. Kratky, *ibid.*, [B], **4**, 401; *A.*, 1132; F. D. Miles and J. Craik, *Nature*, 1929, **123**, 82; *A.*, 126.

but the matter is still under dispute. The complexity of the question is shown by the observations of H. Mark and G. von Susich,[65] who examined the process of mercerisation of cellulose with very intense X-rays, and found that two intermediate compounds are formed in the course of five minutes. The use of very short exposure times will probably prove of great value to chemists in the examination of intermediate phases which it is impossible to isolate.

X-*Ray Diffraction in Liquids.*

In the past year the study of X-ray diffraction in liquids has greatly increased. It is rapidly becoming a standard method of examination. A very complete and satisfactory theory has been developed by J. A. Prins.[66] Two main cases are considered : in the first, which holds for monatomic liquids, the scattering at any angle θ can be expressed by the formula

$$J_{(s)} = \tfrac{1}{2}NA^2 + \tfrac{1}{2}NA^2\int_0^\infty 4\pi r^2 g(r)\,\frac{\sin sr}{sr}\,dr,$$

where A is the amplitude of scattering per atom, $s = \dfrac{4\pi\,\sin\tfrac{1}{2}\theta}{\lambda}$, and $g(r)$ is the distribution function for the scattering centres. If the atoms in the liquid are assumed to be approximately in contact, $g(r)$ can be determined and the diffraction distribution calculated. It agrees very closely with that observed for the diffraction in liquid mercury, which was examined by a very ingenious method in which the X-ray tube and photographic plate moved round the horizontal surface of the liquid. In the case of scattering from polyatomic molecules, account has to be taken of the interference of waves scattered by different parts of the same molecule; the formula now becomes

$$J_{(s)} = \tfrac{1}{2}N\overline{A_s^2} + \tfrac{1}{2}N\overline{A_s^2}\int_0^\infty 4\pi r^2 g(r)\frac{\sin sr}{sr}\,dr,$$

where $\overline{A}_s$ is a function of the molecular structure. For a diatomic molecule, b being the distance between the atoms,

$$\overline{A_s^2} = 2A^2\left[1 + \frac{\sin bs}{bs}\right] \quad\text{and}\quad \overline{A_s^2} = 4A^2\left[\frac{\sin\tfrac{1}{2}bs}{\tfrac{1}{2}bs}\right]^2$$

Calculations on the basis of this formula agree very well with the results obtained for carbon tetrachloride. The formula breaks down if the molecules are anisotropic, and here the question arises as to how far such molecules in the liquid arrange themselves in an ordered way, giving rise to the so-called cybotactic state postulated by G. W. Stewart. This part of the subject is still in dispute. According to

[65] *Naturwiss.*, 1929, **17**, 803.   [66] *Z. Physik*, 1929, **56**, 617; *A.*, 1132.

Prins, long-chain molecules must be roughly parallel, but need not be straight or arranged in layers. There are objections to the assumption of a cybotactic state on the grounds that the large optical scattering which parallel arrangements of molecules would demand is not observed. This is discussed by C. V. Raman and K. S. Krishnan [67] and I. R. Râo.[68] Another case considered is that of solutions, where it is shown that the pattern of the solution does not conserve the maxima of either solute or solvent but gives rise to a pattern dependent on the concentration. Particularly interesting are the results for ionic solutions. Here Prins has shown,[69] by the study of solutions with heavy ions such as those of bromine or iodine, that these arrange themselves in a statistical lattice, owing to their mutual repulsion which is dependent on the concentration. Experimental work on liquids and amorphous solids has largely been carried out by Indian workers, in particular by P. Krishnamurti.[70] A great number of aromatic and aliphatic liquids has been studied. Notable differences have been observed between o-, p-, and m-compounds, and the existence of inner rings points in the cases of a number of acids and alcohols to the existence of association in the liquid state.[71] The work has been done entirely by photographic methods, but it agrees with that of G. W. Stewart [72] by the ionisation method. J. J. Trillat [73] has devised an elegant method of examining surfaces or interfaces by means of X-rays at glancing angles, and shown that long-chain compounds in the solid and the liquid state are definitely oriented in the neighbourhood of the surface.

<div align="right">J. D. BERNAL.
W. A. WOOSTER.</div>

[67] *Proc. Roy. Soc.*, 1928, [A], **117**, 1, 589.

[68] *Indian J. Physics*, 1928, **3**, 1.

[69] *Nature*, 1929, **123**, 84; *A.*, 125; see also H. Shiba and T. Watanabe, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, 187.

[70] *Indian J. Physics*, 1928, **3**, 225, 307, 331, 507; 1929, **4**, 99; *A.*, 246, 751, 989, 1220; V. I. Vaidyanathan, *ibid.*, 1929, **3**, 371, 391; *A.*, 751, 746; K. Banerjee, *ibid.*, p. 399; *A.*, 750; H. F. Hertlein, *Z. Physik*, 1929, **54**, 341.

[71] J. A. Prins, *Nature*, 1929, **123**, 908; *A.*, 746.

[72] *Physical Rev.*, 1929, [ii], **33**, 889; *A.*, 985.

[73] *J. Phys. Radium*, 1929, [vi], **10**, 32; *A.*, 631.

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